

INTERNATIONAL SEARCH REPORT

International Application No

PC 00/03550

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09B29/42 C09D11/00 G03F7/00 G02F1/1335

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09B C09D G03F G02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>EP 0 169 457 A (HOECHST AG) 29 January 1986 (1986-01-29) cited in the application examples 3,20 page 1, line 20 -page 4, line 16 page 5, formula (4c) --- -/--</p>	1,4,5



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

13 December 2000

Date of mailing of the international search report

27/12/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Ketterer, M

INTERNATIONAL SEARCH REPORT

International Application No

PC 00/03550

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Week 9004 Derwent Publications Ltd., London, GB; AN 1990-025870'04! XP002155449 H. YUTAKA: "color filter" & JP 01 303407 A (NIPPON KAYAKU CO. LTD.) cited in the application abstract & JP 01 303407 A (NIPPON KAYAKU CO. LTD.) 7 December 1989 (1989-12-07) page 35, left col., formula 1.</p> <p>---</p>	1
A	<p>PATENT ABSTRACTS OF JAPAN vol. 014, no. 406 (C-0754), 4 September 1990 (1990-09-04) & JP 02 153977 A (MITSUBISHI KASEI CORP), 13 June 1990 (1990-06-13) cited in the application abstract</p> <p>---</p>	1,4,5,24
A	<p>GB 1 359 171 A (CIBA GEIGY AG) 10 July 1974 (1974-07-10) cited in the application examples</p> <p>---</p>	1,4,5
A	<p>EP 0 268 897 A (BASF AG) 1 June 1988 (1988-06-01) examples 106-212</p> <p>---</p>	1,4,5
A	<p>GB 1 271 226 A (ICI LTD.) 19 April 1972 (1972-04-19) cited in the application page 2, line 21 - line 52; claims 1,2,6</p> <p>---</p>	1,2,4,5
A	<p>US 3 926 944 A (BERRIE ALISTAIR HOWARD ET AL) 16 December 1975 (1975-12-16) column 4, line 23 - line 39</p> <p>---</p>	1,4,5
A	<p>DE 951 524 C (FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT) 31 October 1956 (1956-10-31) examples</p> <p>-----</p>	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PC 00/03550

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0169457	A	29-01-1986	DE 3427188 A BR 8503494 A DE 3561743 D IN 164505 A IN 169337 A JP 1757096 C JP 4043114 B JP 61037848 A KR 9309243 B MX 13439 A MX 159995 A US 4659807 A	30-01-1986 15-04-1986 07-04-1988 01-04-1989 28-09-1991 23-04-1993 15-07-1992 22-02-1986 24-09-1993 01-05-1993 23-10-1989 21-04-1987
JP 1303407	A	07-12-1989	NONE	
JP 02153977	A	13-06-1990	JP 2701387 B	21-01-1998
GB 1359171	A	10-07-1974	BE 767179 A CA 965779 A CS 163250 B DE 2123061 A ES 391225 A FR 2091415 A NL 7106678 A US 4067864 A	16-11-1971 08-04-1975 29-08-1975 25-11-1971 01-05-1974 14-01-1972 17-11-1971 10-01-1978
EP 0268897	A	01-06-1988	DE 3639155 A DE 3709567 A JP 63135456 A	26-05-1988 06-10-1988 07-06-1988
GB 1271226	A	19-04-1972	CH 569767 A CH 598335 A CH 599314 A CH 569770 A CH 579622 A CH 539675 A CS 166751 B CS 166755 B CS 166756 B CS 166759 B CS 166760 B CS 166761 B CS 166762 B DE 1948354 A DE 1967137 B ES 371853 A ES 371854 A FR 2019491 A FR 2061420 A JP 50031565 B NL 6914471 A, B, SU 416955 A SU 420186 A SU 368758 A SU 420185 A	28-11-1975 28-04-1978 31-05-1978 28-11-1975 15-09-1976 31-07-1973 29-03-1976 29-03-1976 29-03-1976 29-03-1976 29-03-1976 29-03-1976 29-03-1976 23-04-1970 04-10-1979 16-11-1971 16-11-1971 03-07-1970 18-06-1971 13-10-1975 26-03-1970 25-02-1974 15-03-1974 26-01-1973 15-03-1974
US 3926944	A	16-12-1975	GB 1348641 A US 3936436 A	20-03-1974 03-02-1976

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PC 00/03550

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 951524	C	NONE	

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference SMC 60384/WO	FOR FURTHER ACTION <small>see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.</small>	
International application No. PCT/GB 00/ 03550	International filing date <i>(day/month/year)</i> 18/09/2000	(Earliest) Priority Date <i>(day/month/year)</i> 20/09/1999
Applicant AVECIA LIMITED		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the title,

☐ the text is approved as submitted by the applicant.

☒ the text has been established by this Authority to read as follows:

MONOAZO DYESTUFFS USEFUL FOR COLOUR FILTERS AND INK JET PRINTING

5. With regard to the abstract,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the drawings to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☐ None of the figures.

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Commissioner
 US Department of Commerce
 United States Patent and Trademark
 Office, PCT
 2011 South Clark Place Room
 CP2/5C24
 Arlington, VA 22202
 ETATS-UNIS D'AMERIQUE
 in its capacity as elected Office

Date of mailing (day/month/year) 26 June 2001 (26.06.01)	Applicant's or agent's file reference SMC 60384/WO
International application No. PCT/GB00/03550	Priority date (day/month/year) 20 September 1999 (20.09.99)
International filing date (day/month/year) 18 September 2000 (18.09.00)	
Applicant TALLANT, Neil, Anthony et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:
 20 March 2001 (20.03.01)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer Pascal Piriou Telephone No.: (41-22) 338.83.38
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(19) World Intellectual Property Organization
International Bureau

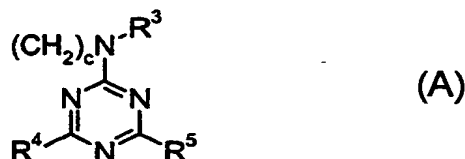
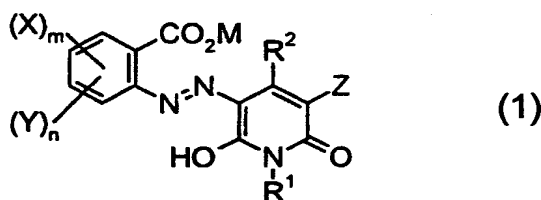


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29 March 2001 (29.03.2001)

PCT

(10) International Publication Number
WO 01/21714 A2

- (51) International Patent Classification⁷: **C09B**
- (21) International Application Number: **PCT/GB00/03550**
- (22) International Filing Date:
18 September 2000 (18.09.2000)
- (25) Filing Language: **English**
- (26) Publication Language: **English**
- (30) Priority Data:
9922136.8 20 September 1999 (20.09.1999) **GB**
- (71) Applicant (for all designated States except US): **AVECIA LIMITED** [GB/GB]; Hexagon House, Blackley, Manchester M9 8ZS (GB).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **TALLANT, Neil, Anthony** [GB/GB]; Hexagon House, P.O. Box 42, Blackley, Manchester M9 8ZS (GB). **MILLARD, Christine** [GB/GB]; Hexagon House, P.O. Box 42, Blackley, Manchester M9 8ZS (GB).
- (54) Title: **COMPOUNDS, COMPOSITIONS AND USE**
- (74) Agents: **MAYALL, John et al.**; Intellectual Property Group, Avecia Limited, Hexagon House, Blackley, P.O. Box 42, Manchester M9 8ZS (GB).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:
— Without international search report and to be republished upon receipt of that report.
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



(57) Abstract: There is described compositions comprising a solvent and at least one compound of Formula (1) in which: R¹ represents H, an optionally substituted C₁₋₈ carbyl derived group, or a group of Formula (A) where: c is from 2 to 6; R³ represents optionally substituted C₁₋₈ carbyl derived group; R⁴ and R⁵ independently represent an optionally substituent; R² represents an optionally substituted C₁₋₈ carbyl derived group; X, Y and Z independently represent H or an optional substituent; M represents H or a cation; m and n independently represent 0, 1 or 2. Also compounds as in Formula (1) providing that at least one of R¹, R², X, Y or Z comprises a group of formula SO₃M or PO₃M₂. These compositions and compounds are useful as the colorants to prepare colour filters for displays.

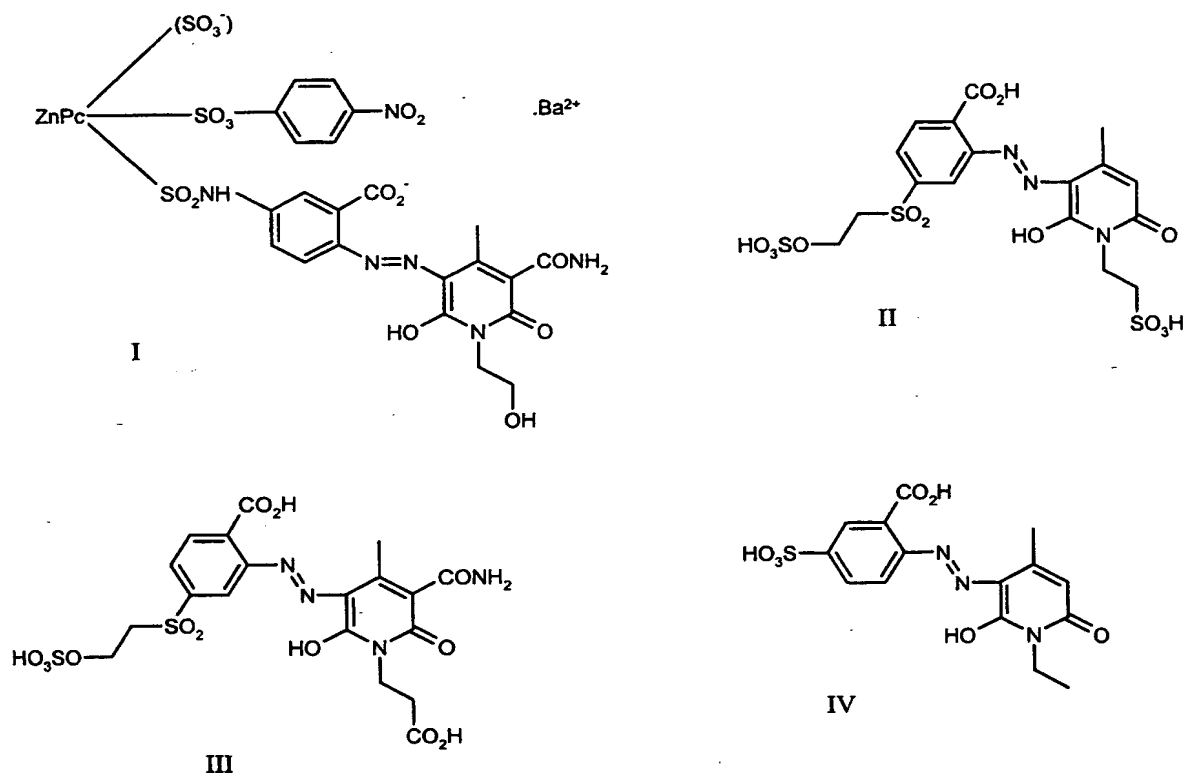
COMPOUNDS, COMPOSITIONS AND USE

This invention relates to compounds, compositions, patterned substrates (such as displays and colour filters) comprising these colorants and to methods of making the same.

The ability to produce brightly coloured patterns or images on substrates, where the colour has high resistance (fastness) to light, water, heat and/or solvents is important in many areas of for instance the electronics and printing industries. Examples of this are in the production of colour filters, in ink-jet printing and in electrophotographic imaging. Thus it is important to discover colorants which can be readily used (and/or formulated into inks for use) in such applications.

Colour filters, alternatively known as optical filters, are a component of coloured liquid crystal displays (LCDs) used as flat screen displays, for example, in small television receivers or portable computers.

Dyes of the following formulae are known:



Dyes of structures II & III are water soluble monoazo pyridones used as cellulose reactive dyes as described in EP 169,457 B1 (Hoechst). The dye of structure IV is described in GB 1,359,171 (Ciba-Geigy), as a dye for wool or cellulosics. The dye of

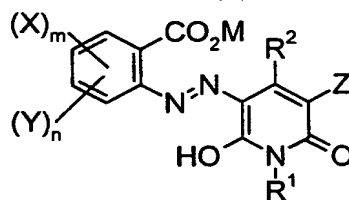
structure I in which a pyridone moiety is bound to a zinc phthalocyanine is described in JP-A 01-303407 (Nippon Kayaku) as a one component green dye for colour filters. This is different from the present invention in which a yellow dye is used as a separate component of a green ink for colour filters. This offers much greater flexibility in adjusting the precise shade of the ink and also is advantageous over zinc phthalocyanines which are less favoured due to poor light fastness.

Known mixtures of copper phthalocyanines and azopyridone yellow dyes (such as the dyes exemplified in JP2701387B2 [Mitsubishi Kasei Corp]) are unsatisfactory for use in colour filter applications because of poor light fastness. However, green colour filters containing azopyridone yellow dyes are significantly brighter than those produced using alternative yellow chromophores such as azobenzenes, azopyrazolones, metallised azo dyes and yellow pigments, which are prevalent in the art.

It is desirable therefore to find improved colorants for use in colour filters, in particular colorants which can be used either alone for example as a yellow or as a yellow component in a mixture (e.g. with cyan colorants such as phthalocyanines). It is a preferred object of a preferred aspect of the invention to discover a green colorant comprising a mixture of one or more yellow colorants with one or more cyan colorants which is of particular use in a colour filter, optionally with improved properties such as light fastness and/or brightness.

The present invention provides azopyridone compounds of use in preparing patterned colored substrates such as colour filters. The compounds give stable inks with advantageous properties. As a preferred aspect of the present invention the applicant has surprisingly discovered certain simple pyridone dyes containing carboxy groups ortho to the azo linkage have a significant advantage in terms of light fastness versus related ortho-sulpho analogues, with no loss in brightness.

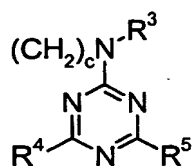
According to the present invention there is provided a composition comprising a solvent and at least one compound of Formula (1)



Formula (1)

in which:

R¹ represents H, an optionally substituted C₁₋₈carbonyl derived group, or a group of Formula A:



Formula A

where:

c is from 2 to 6;

5 R^3 represents H or optionally substituted C_{1-8} carbonyl derived group;

R^4 and R^5 independently represent an optional substituent;

R^2 represents an optionally substituted C_{1-8} carbonyl derived group;

X, Y and Z independently represent H or an optional substituent group;

M represents H or a cation; and

10 m and n independently represent 0, 1 or 2.

The azopyridones of Formula (1) are particularly suitable for use in colour filters, giving very bright yellow films with good light fastness, and as components of ink-jet inks. Conveniently compounds of Formula (1) are not pyridinium pyridones (i.e. Z is not pyridinium).

15 Preferred compounds of Formula (1) are those in which:

R^1 represents H, optionally substituted alkyl, a group of Formula $[\text{R}^9\text{O}]_a\text{R}^6$, or a group of Formula A

R^2 represents alkyl, especially C_{1-4} alkyl more especially methyl, or $\text{CH}_2\text{SO}_3\text{M}$,

20 X and Y independently represent SO_3M , CO_2M , PO_3M_2 , $\text{SO}_2\text{NR}^6\text{R}^7$, CONR^6R^7 , CO_2R^6 , COR^6 , alkyl, alkoxy, NR^6COR^7 , halogen, NO_2 , NR^7R^8 ;

where R^6 and R^7 independently represent H, optionally substituted C_{1-8} alkyl, optionally substituted aryl; and R^8 represents R^6 or a substituted triazinyl group;

Z represents CN, CONH_2 , H or $\text{CH}_2\text{SO}_3\text{M}$;

R^3 represents H or optionally substituted C_{1-8} carbonyl derived group;

25 R^4 and R^5 independently represent halo, SO_3M , NR^6R^7 , OR^6 or SR^7 ;

M represents H, alkali metal ion, ammonium, or a quaternary ammonium cation (hereinafter QAC); more preferably M is Li^+ , Na^+ , K^+ or NH_4^+ ;

m, n is 0, 1 or 2;

a is an integer from 1 to 10, more preferably from 1 to 5, especially 2 to 3; and

30 each R^9 is independently ethylene or propylene:

with the proviso that at least one of R^1 to R^8 , X, Y or Z comprises a group of Formula SO_3M or PO_3M_2 ; and the compound of Formula (1) is other than a compound of Formula II, III or IV as described herein.

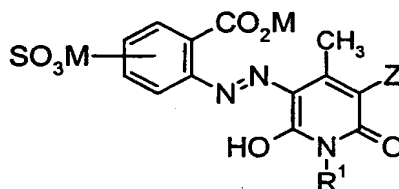
35 Preferred QAC's are those containing C_{1-30} alkyl chains. More preferred QAC cations may be selected from one or more of the following: N,N-diethyl-N-dodecyl-N-benzylammonium; N,N-dimethyl-N-octadecyl-N-(dimethylbenzyl) ammonium; N,N-

dimethyl-N,N-didecyl ammonium; N,N-dimethyl-N,N-didodecyl ammonium; N,N,N-trimethyl-N-tetradecylammonium; N-benzyl-N,N-dimethyl-N-(C₁₂₋₁₈ alkyl)ammonium; N-(dichlorobenzyl)-N,N-dimethyl-N-dodecylammonium; N-hexadecyl pyridinium; N-hexadecyl-N,N,N-trimethylammonium, dodecylpyridinium; N-benzyl-N-dodecyl-N,N-bis(hydroxyethyl)ammonium; N-dodecyl-N-benzyl-N,N-dimethylammonium; N-benzyl-N,N-dimethyl-N-(C₁₂₋₁₈ alkyl)ammonium; N-dodecyl-N,N-dimethyl-N-(1-naphthylmethyl) ammonium and N-hexadecyl-N,N-dimethyl-N-benzylammonium cations.

Suitable QAC cations may also be formed from suitable amines for example from one or more amines selected from: isononylamine, dodecylamine, octadecylamine, didecylamine, didodecylamine, tetradecylamine, hexadecylamine, mixed C₁₂₋₁₈ alkylamines and N-benzyl amines. Preferred amines which may be used to form suitable QAC comprise N-C₁₋₆ alkyl primary amines, N,N-di-C₁₋₆ alkyl secondary amines and N-benzyl amines. Particularly preferred amines comprise methyl and ethyl amine derivatives.

Preferably at least one of R¹, R², X, Y or Z comprises a group of Formula SO₃M or PO₃M₂ where M is independently as represented herein; when n is 0; m is 1; X is a sulpho group para to the azo group; Z is H and R² is methyl then R¹ is other than ethyl and the compound of Formula (1) is other than a compound of Formula II, III or IV as described herein.

More preferred compounds of Formula (1) are of Formula (2):



Formula (2)

in which

Z is CONH₂, CN or H;
R¹ is optionally substituted C₂₋₈alkyl (preferably hydroxy substituted) or a glycol group (for example CH₂CH₂OCH₂CH₃ or CH₂CH₂OCH₂CH₂OH);
with the proviso that if the SO₃M group is in the 4-position of the benzene ring then either R¹ is other than ethyl or Z is other than H.

In general, preferred compounds of the invention are those which give particularly bright yellow films and prints, and are easily synthesised from readily available intermediates. Solubility in an aqueous ink is also desirable, hence compounds of Formula (1) comprise at least one SO₃M or PO₃M₂ group, comprise substituent (e.g. R¹) of C₈ (or less) carbyl-derived groups. To improve solubility optionally R¹ comprises at least one PEG and/or OH group.

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International Bureau



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C09D 11/00, G03F 7/00, G02F 1/1335

C09B 29/42,

(74) Agents: MAYALL, John et al.: Intellectual Property Group, Avecia Limited, Hexagon House, Blackley, P.O. Box 42, Manchester M9 8ZS (GB).

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(22) International Filing Date:
18 September 2000 (18.09.2000)

(25) Filing Language: English

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9922136.8 20 September 1999 (20.09.1999) GB

(71) Applicant (for all designated States except US): AVECIA LIMITED [GB/GB]; Hexagon House, Blackley, Manchester M9 8ZS (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): TALLANT, Neil, Anthony [GB/GB]; Hexagon House, P.O. Box 42, Blackley, Manchester M9 8ZS (GB). MILLARD, Christine [GB/GB]; Hexagon House, P.O. Box 42, Blackley, Manchester M9 8ZS (GB).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

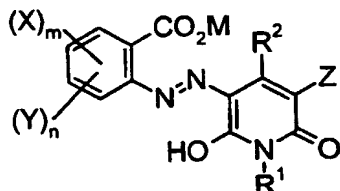
Published:

— with international search report

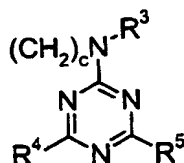
(88) Date of publication of the international search report:
11 October 2001

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: MONOAZO DYESTUFFS USEFUL FOR COLOUR FILTERS AND INK JET PRINTING



(1)



(A)

(57) Abstract: There is described compositions comprising a solvent and at least one compound of Formula (1) in which: R¹ represents H, an optionally substituted C₁₋₈ carbyl derived group, or a group of Formula (A) where: c is from 2 to 6; R³ represents optionally substituted C₁₋₈ carbyl derived group; R⁴ and R⁵ independently represent an optionally substituted C₁₋₈ carbyl derived group; R² represents an optionally substituted C₁₋₈ carbyl derived group; X, Y and Z independently represent H or an optional substituent; M represents H or a cation; m and n independently represent 0, 1 or 2. Also compounds as in Formula (1) providing that at least one of R¹, R², X, Y or Z comprises a group of formula SO₃M or PO₃M₂. These compositions and compounds are useful as the colorants to prepare colour filters for displays.

WO 01/21714 A3

INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/EP 00/03550

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09B29/42 C09D11/00 G03F7/00 G02F1/1335

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09B C09D G03F G02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 169 457 A (HOECHST AG) 29 January 1986 (1986-01-29) cited in the application examples 3,20 page 1, line 20 -page 4, line 16 page 5, formula (4c) --- -/--	1,4,5

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

13 December 2000

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
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Ketterer, M

INTERNATIONAL SEARCH REPORT

Internat'l Application No

PCT/89/00/03550

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Week 9004 Derwent Publications Ltd., London, GB; AN 1990-025870'04! XP002155449 H. YUTAKA: "color filter" & JP 01 303407 A (NIPPON KAYAKU CO. LTD.) cited in the application abstract & JP 01 303407 A (NIPPON KAYAKU CO. LTD.) 7 December 1989 (1989-12-07) page 35, left col., formula 1.</p> <p>---</p>	1
A	<p>PATENT ABSTRACTS OF JAPAN vol. 014, no. 406 (C-0754), 4 September 1990 (1990-09-04) & JP 02 153977 A (MITSUBISHI KASEI CORP), 13 June 1990 (1990-06-13) cited in the application abstract</p> <p>---</p>	1,4,5,24
A	<p>GB 1 359 171 A (CIBA GEIGY AG) 10 July 1974 (1974-07-10) cited in the application examples</p> <p>---</p>	1,4,5
A	<p>EP 0 268 897 A (BASF AG) 1 June 1988 (1988-06-01) examples 106-212</p> <p>---</p>	1,4,5
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INTERNATIONAL SEARCH REPORT

Internal Application No

PCT/89/03550

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/00/03550

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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DE 951524

C

NONE

Compounds of the present invention can be prepared by analogy to any of the methods known in the art, for example as in GB 1,271,226.

According to a further aspect of the present invention there is provided a compound of Formula (1) as hereinbefore defined with the provisos that:

5 at least one of R^1 , R^2 , X, Y or Z comprises a group of Formula SO_3M or PO_3M_2 where M is independently as represented herein;

when n is 0; m is 1; X is a sulpho group para to the azo group; Z is H and R^2 is methyl then R^1 is other than ethyl; and

10 the compound of Formula (1) is other than a compound of Formula II, III or IV as described herein.

Preferences for the substituents in Formula (1) are as hereinbefore defined in relation to the composition. Especially preferred compounds of the invention are of Formula (2) as hereinbefore defined.

15 Preferably the solvent comprises water or more preferably water and one or more water soluble organic solvents.

The viscosity of the composition is preferably less than 100cp, more preferably less than 50cp, especially less than 20cp, more especially less than 15cp and most preferably less than 10cp at 20°C.

20 Preferably the composition has been filtered through a filter having a mean pore size below 10 μm , preferably below 5 μm , more preferably below 2 μm , especially below 0.5 μm . In this way particulate matter is removed which could otherwise block fine nozzles in an ink-jet printer.

25 The composition preferably has a total concentration of divalent and trivalent metal ions, other than those bound to the pigment, below 5000, more preferably below 1000, especially below 100, more especially below 20 parts per million by weight relative to the total weight of the composition. Pure compositions of this type may be prepared by using high purity ingredients and/or by purifying the composition after it has been prepared.

Suitable purification techniques are well known, for example ultrafiltration, reverse osmosis, ion exchange and combinations thereof.

30 When in the formulae herein there is a list of labels (e.g. Ar^1 and Ar^2) or indices (e.g. 'n') which are said to represent a list of groups or numerical values, and these are said to be "independent in each case" this indicates each label and/or index can represent any of those groups listed: independently from each other, independently within each repeat unit, independently within each Formula and/or independently on each group which is substituted; as appropriate. Thus in each of these instances many different
35 groups might be represented by a single label (e.g. Ar^1).

The term 'halo' as used herein signifies fluoro, chloro, bromo and iodo.

The terms 'optional substituent' and/or 'optionally substituted' as used herein (unless followed by a list of other substituents) signifies the one or more of following

groups (or substitution by these groups): carbyl, carboxy, sulpho, phospho, formyl, hydroxy, amino, imino, nitrilo, mercapto, cyano, nitro, halo and/or combinations thereof. These optional groups include all chemically possible combinations in the same moiety of a plurality (preferably two) of the aforementioned groups (e.g. amino and sulphonyl if directly attached to each other represent a sulphamoyl radical).

The term carbyl as used herein denotes any monovalent or multivalent organic radical moiety which comprises at least one carbon atom either solely (e.g. $-C\equiv C-$) or optionally combined with at least one other non-carbon atom (e.g. alkyl, carbonyl etc.). The non-carbon atom(s) may comprise any elements other than carbon (including any chemically possible mixtures or combinations thereof) that together with carbon can comprise an organic radical moiety. Preferably the non-carbon atom is selected from at least one hydrogen and/or heteroatom, more preferably from at least one: hydrogen, phosphorus, halo, nitrogen, oxygen and/or sulphur, most preferably from at least one hydrogen, nitrogen, oxygen and/or sulphur. Carbyl groups include all chemically possible combinations in the same group of a plurality (preferably two) of the aforementioned carbon and/or non-carbon atom containing moieties (e.g. alkoxy and carbonyl if directly attached to each other represent an alkoxy carbonyl radical).

Preferably 'carbyl-derived' moieties comprise at least one of the following carbon containing moieties: alkyl, alkoxy, alkanoyl, carboxy, carbonyl, formyl and/or combinations thereof; optionally in combination with at least one of the following heteroatom containing moieties: oxy, thio, sulphinyl, sulphonyl, amino, imino, nitrilo and/or combinations thereof.

The term 'hydrocarbyl' as used herein (which is encompassed by the term 'carbyl-derived') denotes any radical moiety which consists only of at least one hydrogen atom and at least one carbon atom. A hydrocarbyl group may however be optionally substituted.

More preferably 'hydrocarbyl derived' moieties comprise one or more of the following carbon containing moieties: alkyl, aryl, alkaryl and/or combinations thereof. The term 'aryl' as used herein signifies a radical which comprises an aromatic hydrocarbon ring, for example phenyl, naphthyl, anthryl and phenanthryl radicals. The term 'alkyl' or its equivalent (e.g. 'alk') as used herein may be readily replaced, where appropriate, by terms denoting a different degree of saturation and/or valence e.g. moieties that comprise double bonds, triple bonds, and/or aromatic moieties (e.g. alkenyl, alkynyl and/or aryl) as well as multivalent species attached to two or more substituents (such as alkylene).

Any radical group mentioned herein as a substituent refers to a monovalent radical unless otherwise stated. A group which comprises a chain of three or more atoms signifies a group in which the chain may be straight or branched or the chain or part of the chain may form a ring. For example, an alkyl group may comprise: propyl which includes n-propyl and isopropyl; butyl which includes n-butyl, sec-butyl, isobutyl and tert-butyl; and an alkyl group of three or more carbon atoms may comprise a cycloalkyl group. The total

number of certain atoms is specified herein for certain substituents, for example C_{1-n} alkyl, signifies an alkyl group having from 1 to n carbon atoms. Preferred alkyl groups in compounds of Formulae (1) and (2) may be branched or straight chain and preferred branched chain alkyl groups are α - branched alkyl groups.

5 Advantageously the optional substituents and/or carbyl derived groups which may be present in Formula (1) herein may be each independently selected from: carboxy, sulpho, phospho, nitro, bromo, chloro fluoro, alkyl (especially C_{1-4} alkyl) alkoxy (especially C_{1-4} alkoxy), hydroxy, sulphamoyl, amine (especially $-NHR^{10}$ and $NR^{10}Ar$), mercapto, thioalkyl (especially C_{1-4} thioalkyl), cyano, ester (especially $OCOR^{10}$ or $COOR^{10}$) and amide (especially $CONHR^{10}$ and $NHCOR^{10}$);

10 where R^{10} is H or optionally substituted C_{1-6} alkyl (especially H or C_{1-4} alkyl) and Ar is an optionally substituted aromatic ring (especially a benzene ring).

 More preferred optional substituents and/or carbyl derived groups in Formula (1) are selected from SO_3M , CO_2M , PO_3M_2 , Cl, Br, F, OH, C_{1-4} alkyl, C_{1-4} alkoxy, $CONH_2$,
15 SO_2NH_2 , $OCO(C_{1-4}alkyl)$, $COO(C_{1-4}alkyl)$, $NHAr$ and $NHCO(C_{1-4}alkyl)$, where M and Ar are as defined herein.

 Certain compounds and/or moieties therein (such as repeat units), which comprise the present invention may exist in many different forms for example at least one form from the following non-exhaustive list: salts (e.g. with organic and/or inorganic acids
20 and/or bases including acid and/or base addition salts); isomers, stereoisomers, enantiomers, diastereoisomers, geometric isomers, tautomers, conformers, zwitterions, forms with regio-isomeric substitution, isotopically substituted forms, polymorphs, polymeric configurations, tactic forms, interstitial forms, complexes, chelates, clathrates, interstitial compounds, non-stoichiometric complexes, stoichiometric complexes, ligand
25 complexes, organometallic complexes, solvates, isotopic forms, mixtures thereof and/or combinations thereof within the same species. The present invention preferably comprises all such forms of compounds, polymers, moieties therein, any compatible mixtures thereof and/or any combinations thereof, which comprise the present invention, preferably those which are effective in IJP and/or colour filters.

30 Salts of Formula (1) may be formed from one or more organic and/or inorganic bases. Preferred salts of Formula (1) are soluble in water.

 The inks preferably contain from 1 to 10, more preferably from 1 to 6, especially from 1 to 3, more especially 1 compound of Formula (1).

 The compounds of Formula (1) are preferably soluble in water. However, they
35 may be modified to be soluble in organic solvents by use of a QAC as the counter ion, where QAC is as hereinbefore defined.

 The compounds of Formula (1) may be prepared by any suitable method known in the prior art.

The composition may contain further compounds other than those of Formula (1), for example to modify the colour or brightness of the ink.

5 The compounds of Formula (1) may be used individually as part of a YMC (yellow, magenta, cyan) colour filter, or mixed with other compounds as the red or green component of an RGB (red, green, blue) colour filter. The arrangement of pixels could be any of those known in the art (stripe, mosaic, delta) and the filters would be suitable for displays, especially LCD's, and solid state imaging devices.

Use of the compounds of Formula (1) gives filters with very good fastness properties and brighter than those in the prior art.

10 The compounds may also be used in an ink-jet printing ink to give bright yellow prints with good fastness properties.

It is another object of the present invention to provide improved inks for processes for forming film coatings, that overcome some or all of the disadvantages of the prior art as discussed above, as well as products made and coated by processes using such inks (in particular colour filters). In particular there is provided a composition according to the first aspect of the invention which is a green, red or yellow ink suitable for use in any of these processes.

20 Therefore according to another aspect of the present invention, there is provided an ink containing a compound of Formula (1) for use in any process for preparing a patterned, cross-linked, polymer, film coating on a substrate.

It is particularly preferred that the inks of the current invention are used in processes to manufacture a colour filter. These processes may comprise or consist of steps known in methods for producing colour filters (with colorants other than the novel compounds of the present invention). Such processes are well known in the art and include various printing, photolithographic, photographic, electrodeposition, laser ablation and thermal transfer processes. Examples of suitable processes are described below and in the following references, but it is to be understood that the invention is not limited to these processes:

30 "Reliability Improvements of Dichromated Gelatin Color Filters for TFT-LCD's", A. Endo, E. Hirose, T. Sato, S. Otera, N. Chiba, Polym. Mater. Sci. Eng., 1990, 63, 472-6.

"Process and Material for Color Filter Preparation in Liquid Crystal Display", H. Aruga, J. Photopolym. Sci. Technol., 1990, 3, 9-16.

"Color Filter for Liquid Crystal Display", S. Okazaki, Trans. Inst. Electron. Inf. Commun. Eng., Sect. E, 1988, E71, 1077-9.

35 P. Gregory, Chapter 2 "Micro Color Filters" in "High-Technology Applications of Organic Colorants", Kluwer Academic/Plenum Publishers, 1991.

"Color Filters for LCDs", K. Tsuda, Displays, 1993, 14, 115-24.

"Printing Color Filter for Active Matrix Liquid Crystal Display Color Filter", K. Mizuno, S. Okazaki, Jpn. J. Appl. Phys., Part 1, 1991, 30, 3313-17.

EP 661350 (=US 5,608,091) (Nippon Shokubai)

EP 833203 (Nippon Shokubai)

It will be appreciated that where the compounds described are not water soluble, the processes described in the references may need appropriate modification to allow the use of the compositions and compounds of the present invention. Alternatively, where the colorants described are solvent soluble dyes, compositions and compounds of the present invention may be used by modification of their solubility in organic solvents through appropriate choice of the counter ion as described previously.

A typical process for preparing a patterned, cross-linked, polymer, film coating on a substrate comprising the steps of

- (a) applying to the substrate simultaneously and/or sequentially in any order:
 - (i) one or more cross-linkable polymer precursor(s);
 - (ii) optionally one or more additional cross-linker(s) capable of cross-linking the precursor(s) for the polymer(s); and
 - (iii) one or more compound(s) of Formula (1) optionally with one or more other colorant(s);
- (b) optionally patterning one or more non cross-linked film(s) of component (i); component (ii); component (iii) and/or mixture(s) thereof, optionally before application of further components; and
- (c) initiating cross-linking the mixture of components (i), (ii) in situ, to form an optionally patterned, cross-linked polymeric film coating on the substrate.

Preferably the application method in step (a) comprises applying an ink comprising both components (i) and (ii).

It is also preferred that the polymer precursor(s) in step (a) (i) above comprise water dissipatable polymer precursor(s). It is especially preferred that these water dissipatable polymer precursor(s) comprise acrylic polymer precursor(s).

A process for which the present invention is particularly suitable is a printing process, especially an ink-jet printing (IJP) process.

Preferably the printing process used is thermal or piezo IJP. The principles and procedures for ink jet printing are described in the literature for example in High Technology Applications of Organic Colorants, P. Gregory, Chapter 9 ISBN 0-306-43637-X.

Other suitable printing methods comprise: flexographic printing; off-set printing [e.g. as described in JP-A-10(98)-088055 (Sumitomo Rubber)] lithographic printing; gravure printing; intaglio printing; dye diffusion thermal transfer; screen and/or stencil printing [e.g. as described in WO 97-048117 (Philips Electronics)] and/or using 'typographic ink imaging pins' (e.g. as described in WO 97-002955 (Corning Inc.)).

Preferred methods of applying the polymer precursor and compound of Formula (1) to the substrate comprise one or more of the following:

1) print onto the substrate (advantageously by IJP) a mixture comprising the polymer precursor which is thermally cross-linkable and the colorant; and thereafter curing the mixture in situ (e.g. as described in the applicant's co-pending application GB 9824818.0).

2) Apply to the substrate a polymer precursor which is an anionic colourable photosensitive resin, and then exposing the resin to UV light via a mask to either make the exposed portions, which correspond to the pixels accept colorant; or harden the resin at the exposed portions, which correspond to the black matrix, to make it resistant to colorant; and print onto the resin (advantageously by IJP) a solution of the colorant. [e.g. as described in EP 0703471(Canon)]:

An additional method of applying the ink is by a photolithographic process. This may involve either:

1) Apply to a substrate a polymer precursor which is an anionic colourable photosensitive resin; and then expose the resin to radiation (e.g. UV light) through a patterned mask, develop the substrate to remove unexposed portions of the resin, optionally heat to further set the resin, then dip the substrate into an aqueous solution of the colorant. [e.g. as described in US 5,190,845 (Nippon Kayaku)]

2) Apply to a substrate an ink containing a photosensitive resin and the colorant; and then expose the resin to radiation (e.g. UV light) through a patterned mask, develop the substrate to remove either the exposed or unexposed portions of the resin and optionally heat to further set the resin [e.g. as described in EP 564237 (Mitsui Toatsu)]

3) Apply to a substrate a non-photosensitive ink containing the colorant and a thermally cross-linkable resin; then apply an ink containing a photosensitive resin over this coloured film; expose the photosensitive resin to radiation (e.g. UV light) through a patterned mask; develop the substrate to remove either the exposed or unexposed portions of the photosensitive resin and the corresponding portions of the coloured film beneath, heat to thermally cure the coloured polymeric film and optionally strip the photosensitive resin that remains [e.g. as described in US 5,176,971 (Kyodo Printing) and WO 88/05180 (Brewer Science Inc.)]

In 1) the photosensitive resin may be either a natural polymer such as gelatin or casein which has been photosensitised by the addition of for example ammonium dichromate, or may be a synthetic polymer.

In 2) and 3) the photosensitive resins used may be of either the positive or negative type. In the positive type, the solubility of the resin in a developing solution increases on exposure to radiation; in the negative type the solubility of the resin in a developing solution decreases on exposure to radiation.

In the laser ablation method, an ink containing a compound of Formula (1) and a (optionally thermally curable) non-photosensitive resin is applied to the substrate, then portions of the substrate are irradiated with a laser beam to selectively remove the ink in

those areas through vaporisation and the remaining ink is optionally heated to thermally cure the resin [e.g. as described in JP10274709 (Sekisui Chem Ind.)]

In these processes the inks may be applied to the substrate by any known coating method including spin-coating, bar-coating, dip-coating, curtain-coating, roller-coating and electropray.

The process of the present invention can be used to give optionally patterned, optionally transparent films and coatings on substrates in general, including substrates which are not transparent. Accordingly the present invention includes a process for preparing polymeric film coatings for substrates in general not just colour filters.

The cross-linked polymeric film coating may be formed on a substrate to which the coating will bond, adhere, absorb or fuse. Preferably (e.g. if the process of the present invention is used to manufacture a colour filter) the substrate is transparent. Suitable transparent substrates include glass; plastics films and plates such as those of polyvinylalcohol, polyester, polyvinylchloride, polyvinylfluoride, polycarbonate, polystyrene, polyamide or polyimide. The substrate may be flexible or may be a flat panel (e.g. as used in many LCD displays). A preferred substrate is glass.

The substrates may be pre-treated to improve bonding, adhesion, absorption, fusion or spreading of the cross-linked polymeric coating on the substrate. Suitable pre-treatments include plasma etching in which the substrate is placed in an oxygen atmosphere and subjected to an electrical discharge or application of an adhesion promoter such as a silane.

An ink suitable for manufacture of a colour filter according to the present invention may be made by any method known in the art and comprise: one or more compounds(s) of Formula (1), one or more solvents and optionally other formulating agents. The inks may in addition contain precursor(s) for cross-linked polymer(s), one or more cross-linker(s) capable of cross-linking the precursor(s), optionally one or more non cross-linkable polymer(s) for improving the film-forming ability of the inks or the properties of the final films and (as appropriate for chemically or photochemically initiated systems) either a radical source, a photopolymerisation initiator or a dissolution inhibitor. An ink coloured in one of the desired colours can be produced with compounds of the present invention and optionally one or more other colorants, typically either yellow, green or red.

Preferably the optionally patterning method in step (b) of the process of the present invention uses electromagnetic radiation, more preferably UV radiation. Optionally to produce a colour filter the pattern formed may comprise of a multiplicity of discrete filter regions (pixels) on a transparent substrate via a single pass ink-jet printing process. Optionally, the transparent substrate has previously been subdivided into discrete pixel regions by any method known in the art (for example formation of a black matrix by photolithography).

The steps of the process of the present invention described herein may be followed for each of the desired colours to form a multi-colour optical filter structure so that the filter structure finally comprises the transparent substrate and a single layer of differently coloured pixels arranged in triads or in any desired groups, each consisting of a predetermined number of differently coloured pixels.

The inks of the present invention are particularly useful for forming the green and red pixels of an additive (red, green and blue [RGB]) colour filter and for forming the yellow pixels of a subtractive (yellow, magenta and cyan [YMC]) colour filter.

A further aspect of the invention provides a process for printing an image on a substrate comprising applying thereto an ink according to another aspect of the present invention, preferably by printing, more preferably by means of an ink jet printer. Preferably the ink comprises solvent (preferably aqueous) and a compound of Formula (1) as described herein.

The ink jet printer preferably applies the ink to the substrate in the form of droplets which are ejected through a small nozzle onto the substrate. Preferred ink jet printers are piezoelectric ink jet printers and thermal ink jet printers. In thermal ink jet printers, programmed pulses of heat are applied to the ink in a reservoir (e.g. by means of a resistor adjacent to the nozzle) thereby causing the ink to be ejected in the form of small droplets directed towards the substrate during relative movement between the substrate and the nozzle. In piezoelectric ink jet printers the oscillation of a small crystal causes ejection of the ink from the nozzle. The term ink-jet printer denotes any device which could use an IJP technique to produce an image.

A further aspect of the present invention provides a substrate which has applied thereon an ink of the present invention as defined herein and/or which has been prepared by the process of the present invention also as defined herein.

The substrate, which is optionally transparent, preferably comprises plastic, metal, glass, paper, an overhead projector slide and/or a textile material. More preferably for a colour filter the substrate is glass. Preferred textile materials for ink jet printing are cotton, polyester and blends thereof. When the substrate is a textile material the process for printing an image thereon according to the invention preferably further comprises the step of heating the resultant printed textile, preferably to a temperature of 50°C to 250°C.

According to a further feature of this invention there is provided a colour filter comprising red, green and blue filter elements, or yellow, magenta and cyan filter elements, characterised in that the colour filter carries a compound of Formula (1). Preferably the color filter further comprises a coloured cross-linked polymeric coating on a transparent substrate and/or a transparent, coloured, cross-linked, polymer coating on a substrate prepared by the processes according to the present invention.

More preferably the substrate or colour filter comprises an array of coloured trichromatic elements in which the trichromat is selected from: a red, green and blue trichromat; and a cyan, magenta and yellow trichromat.

Preferably the substrate or colour filter has utility as a component for a coloured display.

A further feature of the invention comprises a display containing a substrate or colour filter prepared according to the present invention. Preferably the display comprises a liquid crystal display.

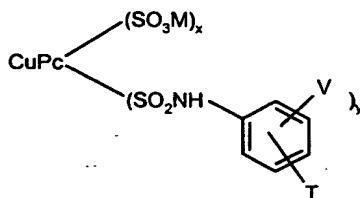
A further feature of the present invention provides a cartridge suitable for use in an ink jet printer containing an ink according to the invention. Also there is provided an ink jet printer containing an ink according to the invention.

The compounds of the present invention are particularly useful as yellow dyes which form particularly good green colorants when combined with a further cyan dye or pigment. Such compositions are particularly useful to produce a green colour filter

For the purposes of the present invention the term "colorant" as used herein denotes perceptible and/or emissive materials. The term "perceptible material" as used herein includes all dyes and/or pigments and denotes materials which absorb radiation substantially in that part of the electromagnetic (EM) spectrum which encompass the infra red (IR); visible and/or ultraviolet (UV) regions, preferably in a region where the radiation wavelength [λ] is from about 200 nm to about 800 nm, more preferably in the visible region which is detectable by the normal, unaided human eye. The term "emissive material" as used herein denotes a material which is capable of emitting radiation, preferably EM radiation, more preferably radiation in the IR, visible and/or UV regions of the EM spectrum. Examples of emissive materials comprise fluorescent, phosphorescent and/or radioactive materials.

Therefore broadly in another aspect of the present invention there is provided a coloured composition comprising a compound of Formula (1) or (2) (as described herein) together with one or more cyan or green dye(s) and/or one or more cyan or green pigments(s).

Preferably the cyan or green dye comprises a water soluble metal phthalocyanine, more preferably a copper, zinc, aluminium and/or nickel phthalocyanine. Preferably the composition of the present invention comprises a cyan dyes of Formula (3)



Formula (3)

in which:

T represents H or an optional substituent, preferably H, alkyl, alkoxy, CO₂M, SO₃M;

V represents CO₂M, SO₃M or PO₃M₂, especially meta-CO₂M

5 x and y independently represent from 0 to 4, preferably from 1 to 3; and

x + y is from 3 to 5, preferably 4;

where M is as given herein for compounds of Formula (1) herein.

Where the cyan or green colorant is a pigment, preferred pigments include C.I. Pigment Green 7 and C.I. Pigment Green 36.

10 The colorants of the present invention may also be used as shading components in combination with red, magenta and/or orange colorants to produce good red colorants which are useful for producing a red colour filter.

Therefore, in another aspect of the present invention there is provided a coloured composition comprising a compound of Formula (1) (as described herein) together with one or more red, magenta and/or orange colorant(s), [e.g. dye(s) and/or pigment(s)].

15 It is also to be understood that one or more further yellow colorant(s), [e.g. dye(s) and/or pigment(s)] other than those of the current invention, may be present in the ink for the purpose of adjusting the shade or enhancing the fastness properties of the ink and the resultant film or image produced using the ink.

20 Apart from the colorants of the present invention of Formula (1) and (2), compositions, inks, colour filters and processes of the present invention may comprise at least one further colorants to form a colorant mixture.

The further colorants (as well as colorants of the present invention) are preferably compatible with the resultant cross-linked polymer coatings, i.e. the resultant cured films have high transparency. Where the colorant is a dye, preferably the colorant is insoluble in organic solvents and soluble in water, for example the colorant may contain sulpho, phospho or carboxy groups.

25 If the colorant used is not soluble in the solvent used for the ink, the colorant is preferably present as a fine dispersion, prepared by for example milling the colorant in a solvent in a horizontal shaker in the presence of glass or metal beads and a dispersant. Suitable dispersants may comprise an anionic type (for example lignosulphonates and other sulphonated aromatic species) or a non-ionic type (for example alkylene oxide adducts).

30 Useful classes of further colorants include azos (including metallised azos), anthraquinones, phthalocyanines, perylenes, quinacridones, diketopyrrolopyrroles, pyrrolines, thiophenedioxides, triphenodioxazines, methines, benzofuranones, benzodifuranones, coumarins, indoanilines, benzenoids, xanthenes, triphenylmethanes, nitros, nitrosonaphthols, phenazines, solvent soluble sulphur dyes, quinophthalones, pyridones, aminopyrazoles, pyrrolidines, pyrroles, styrylics, maleimides,

triphenazonaphthylamines, styryls, dithienes, azomethines, cyanines, indanthrones, benzimidazolones, isoindolinones, isoindolines and azoics.

The Colour Index International lists suitable dyes and pigments for use as further colorants such as acid dyes, direct dyes, basic dyes, reactive dyes, solvent dyes, disperse dyes and pigments and further examples of acid dyes are given in the Colour Index, 3rd Edition, Volume 1, pages 1003 to 1561, further examples of direct dyes are given in Volume 2, pages 2005 to 2478, further examples of basic dyes are given in Volume 1, pages 1611 to 1688, further examples of reactive dyes are given in Volume 3 pages 3391 to 3560, further examples of solvent dyes are given in Volume 3, pages 3563 to 3648, further examples of disperse dyes are given in Volume 2, pages 2479 to 2742, and further examples of pigments are given in Volume 3 pages 3267 to 3390. These colorants are included herein by reference.

Preferably the further colorant(s) is selected from at least one cyan, green, red, magenta and/or orange colorant which is a dye or a pigment.

Subject to the provisos herein, generally preferred colorants are pigments; or dyes which have substituent groups which aid the solubility of the dye(s) in liquid media used in the process or which aid the solubility of the dye(s) in the final cross-linked polymer matrix.

Preferably the composition is an the ink comprising:

(a) from 0.01 to 30 parts of a compound of Formula (1); and

(b) from 70 to 99.99 parts of a liquid medium or a low melting point solid medium;

wherein all parts are by weight and the number of parts of (a) + (b)=100.

The number of parts of component (a) is preferably from 0.1 to 20, more preferably from 0.5 to 15, and especially from 1 to 5 parts. Compound A is preferably an IJP effective compound of Formula (1) more preferably of Formula (2). The number of parts of component (b) is preferably from 99.9 to 80, more preferably from 99.5 to 85, especially from 99 to 95 parts.

When the medium is a liquid, preferably component (a) is completely dissolved in component (b). Preferably component (a) has a solubility in component (b) at 20°C of at least 10%. This allows the preparation of concentrates which may be used to prepare more dilute inks and reduces the chance of the colorant precipitating if evaporation of the liquid medium occurs during storage.

Preferred liquid media include water, a mixture of water and a water miscible organic solvent.

When the medium comprises a mixture of water and an organic solvent, the weight ratio of water to organic solvent is preferably from 99:1 to 1:99, more preferably from 99:1 to 50:50 and especially from 95:5 to 80:20. The liquid medium may comprise water and preferably two or more, more preferably from 2 to 8, water-soluble organic solvents.

The water-miscible organic solvent(s) may comprise any of the following and/or mixtures thereof: C₁₋₆-alkanols, preferably methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, n-pentanol, cyclopentanol and/or cyclohexanol; amides, preferably linear amides, for example dimethylformamide and/or dimethylacetamide; ketones and/or ketone-alcohols, preferably acetone, methyl ether ketone, cyclohexanone and/or diacetone alcohol; water-miscible ethers, preferably C₂₋₄ethers, tetrahydrofuran and/or dioxane; diols, preferably alkylene glycols containing a C₂-C₆ alkylene group; more preferably C₂₋₁₂diols (for example pentane-1,5-diol, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol); thioglycols preferably thiodiglycol; oligo- and/or poly-alkyleneglycols (for example diethylene glycol, triethylene glycol, polyethylene glycol and/or polypropylene glycol); triols, preferably glycerol and/or 1,2,6-hexanetriol; lower alkyl glycol and polyglycol ethers, preferably C₁₋₄alkyl ethers of diols or monoC₁₋₄alkyl ethers of C₂₋₁₂diols: {for example 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)ethanol, 2-(2-butoxyethoxy)ethanol, 3-butoxypropan-1-ol, 2-[2-(2-methoxyethoxy)ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)ethoxy]ethanol and/or ethyleneglycol monoallyl ether}; cyclic amides, preferably optionally substituted pyrrolidones (for example 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, caprolactam and/or 1,3-dimethylimidazolidone); cyclic esters, preferably caprolactone; sulphoxides, preferably dimethyl sulphoxide and/or sulfolane.

More preferred water-soluble organic solvents are selected from: cyclic amides (for example 2-pyrrolidone, dimethyl pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone N-(2-hydroxyethyl)-2-pyrrolidone and mixtures thereof); diols, (for example 1,5-pentane diol, ethyleneglycol, thiodiglycol, diethyleneglycol and triethyleneglycol); C₁₋₆alkyl ethers of diols (for example 2-methoxy-2-ethoxy-2-ethoxyethanol); C₁₋₆-alkyl mono ethers of C₂₋₆-alkylene glycols; C₁₋₆-alkyl mono ethers of poly(C₂₋₆-alkylene glycols); and mixtures thereof.

A preferred liquid medium comprises:

(a) from 75 to 95 parts water; and

(b) from 25 to 5 parts in total of one or more solvents selected from:

diethylene glycol, 2-pyrrolidone, thiodiglycol, N-methylpyrrolidone, cyclohexanol, caprolactone, caprolactam and pentane-1,5-diol;

where the parts are by weight and the sum of the parts (a) + (b) = 100.

Another preferred liquid medium comprises:

(a) from 60 to 80 parts water;

(b) from 2 to 20 parts diethylene glycol; and

(c) from 0.5 to 20 parts in total of one or more solvents selected from:

2-pyrrolidone, N-methylpyrrolidone, cyclohexanol, caprolactone, caprolactam, pentane-1,5-diol and thiodiglycol;

where the parts are by weight and the sum of the parts (a) + (b) + (c) = 100.

When the liquid medium comprises an organic solvent free from water, (i.e. less than 1% water by weight) the solvent preferably has a boiling point of from 30° to 200°C, more preferably of from 40° to 150°C, especially from 50 to 125°C. The organic solvent may be water-immiscible, water-miscible or a mixture of such solvents. Preferred water-immiscible organic solvents comprise any of those described above and mixtures thereof. Preferred water-immiscible solvents comprise aliphatic hydrocarbons; esters (for example ethyl acetate) chlorinated hydrocarbons (for example dichloromethane), ethers (for example diethyl ether) and mixtures thereof.

When the liquid medium comprises a water-immiscible organic solvent, preferably it comprises a polar solvent (for example a C₁₋₄alkanol) to enhance the solubility of the dye in the liquid medium. It is especially preferred that where the liquid medium is an organic solvent free from water it comprises a ketone (especially methyl ethyl ketone) and/or an alcohol (especially a C₁₋₄alkanol, more especially ethanol or propanol).

The organic solvent free from water may be a single organic solvent or a mixture of two or more organic solvents. It is preferred that when the medium is an organic solvent free from water it is a mixture of 2 to 5 different organic solvents. This allows a medium to be selected which gives good control over the drying characteristics and storage stability of the ink.

Ink media comprising an organic solvent free from water are particularly useful where fast drying times are required and particularly when printing onto hydrophobic and non-absorbent substrates, for example plastics, metal and glass.

Preferred low melting solid media have a melting point in the range from 60°C to 125°C. Suitable low melting point solids include long chain fatty acids or alcohols, preferably those with C₁₈₋₂₄ chains, and sulphonamides. The compound of Formula (1) may be dissolved in the low melting point solid or may be finely dispersed in it.

The ink may also contain additional components conventionally used in inks for IJP, for example viscosity and surface tension modifiers, corrosion inhibitors, biocides, fogging reducing additives and surfactants which may be ionic or non-ionic.

In a further aspect of the present invention there is provided a general purpose ink optionally for use in preparing a colour filter, the ink comprising a fluid medium, and one or more compounds of Formula (1) herein. The precursor(s), cross-linker(s) and colorant(s) are as defined previously.

Preferably inks according to the invention are prepared by mixing together (i) a solution of the compound(s) of Formula (1) and optionally water.

The amount of the compound(s) of Formula (1) and solvent contained in the ink will vary according to the depth of shade required. Typically, however, the ink will comprise

(a) from 0.5 to 15 parts, more preferably 0.8 to 10 parts, especially 1 to 8 parts in total of one or more compounds of Formula (1);

- (b) from 0 to 90 parts, more preferably from 50 to 80 parts of water; and
- (c) from 0 to 90 parts, more preferably 0 to 60 parts of one or more water miscible organic solvent(s); and
- (d) other ingredients from 0 to 50 parts, more preferably 0 to 30;

5 where all parts are by weight and the total number of parts of (a) + (b) + (c) + (d) add up to 100.

The water-miscible solvent may be one or more of those described herein, preferably with a solubility in water at 20°C of more than 50g/l.

10 Instead of parts (b) and (c) [the water and water-miscible organic solvent(s)] the ink may comprise one or more water-immiscible organic solvent(s).

Suitable water-immiscible organic solvents include aromatic hydrocarbons, e.g. toluene, xylene, naphthalene, tetrahydronaphthalene and methyl naphthalene; chlorinated aromatic hydrocarbons, e.g. chlorobenzene, fluorobenzene, chloronaphthalene and bromonaphthalene; esters, e.g. butyl acetate, ethyl acetate, methyl benzoate, ethyl benzoate, benzyl benzoate, butyl benzoate, phenylethyl acetate, butyl lactate, benzyl lactate, diethyleneglycol dipropionate, dimethyl phthalate, diethyl phthalate, dibutyl phthalate, di (2-ethylhexyl) phthalate; alcohols having six or more carbon atoms, e.g. hexanol, octanol, benzyl alcohol, phenyl ethanol, phenoxy ethanol, phenoxy propanol and phenoxy butanol; ethers having at least 5 carbon atoms, preferably C₅₋₁₄ ethers, e.g. anisole and phenetole; nitrocellulose, cellulose ether, cellulose acetate; low odour petroleum distillates; turpentine; white spirits; naphtha; isopropylbiphenyl; terpene; vegetable oil; mineral oil; essential oil; and natural oil; and mixtures of any two or more thereof.

20 The water-immiscible solvent preferably has a solubility in water at 20°C of up to 50g/l.

A further feature of the invention provides a composition comprising a water-dissipatable polymer and a compound of Formula (1). In these compositions the preferred water-dissipatable polymers and dyes are as described in in the following co-pending patent applications WO95/34204, WO99/50326, WO99/50362, WO99/50361, 30 WO00/29493, WO00/37575. These applications are hereby incorporated by reference. These applications are hereby incorporated by reference.

Such compositions may be dissipated in water and optionally mixed with further ingredients to give an ink, for example with one or more organic solvents.

35 The other ingredients may comprise one or more formulating agents conventionally used in inks for example to improve the solubility of colorant in the ink and/or to improve the flow and handling properties of the ink. Thus for example the ink may comprise one or more: humectant(s); rheological agent(s) [such as viscosity modifier(s) and/or surface tension modifier(s), for example wax(es) (e.g. beeswax) and/or clay(s) (e.g. bentonite)]; corrosion inhibitor(s), biocides (such as those available

commercially from Avecia Limited under the trade name Proxel GXL or from Rohm and Haas under the trade name Kathon); fungicide(s); kocation reducing additives; IR absorber(s) (such as that available commercially from Avecia Limited under the trade name Projet 900NP); fluorescent brightener(s), (such as C.I. Fluorescent Brightener 179);
5 and surfactant(s) (which may be ionic or non-ionic and include surface active agent(s) wetting agent(s) and/or emulsifier(s) such as those described in McCutcheon's Emulsifiers and Detergents 1996 International Edition or in Surfactants Europa 3rd Edition 1996 each of which is incorporated herein by reference).

The ink may also comprise radical scavengers and/or UV absorbers to help
10 improve light and heat fastness of the ink and resultant colour filter. Examples of such additives include: 2-hydroxy-4-methoxy-5-sulfobenzophenone; hydroxy phenylbenzotriazole; 4-hydroxy-TEMPO and transition metal complexes (such as nickel complexes of thiocarbamic acids). These additives are used typically in an amount from 30% to 60% by weight of the colorant, and are further described in "The Effect of
15 Additives on the Photostability of Dyed Polymers", Dyes and Pigments, 1997, 33(3), 173-196 and JP-A- 04-240603 (Nippon Kayaku).

For an aqueous ink, the ink preferably has a pH from 3 to 12, more preferably from 4 to 11. The pH selected will depend to some extent on the desired cation for the colorant and the method of application. The desired pH may be obtained by the addition
20 of a pH adjusting agent such as an acid, base or pH buffer. The amount of pH adjuster used will vary according to the desired pH of the ink, but typically a base may be present in an amount of up to 30 %. Where a liquid(s) is added to the mixture the printed substrate may be dried by heating or by air drying at ambient temperature to evaporate the liquid before the coating is cured or during curing.

25 Examples of suitable formulations of polymer precursor and colorant which may be used in the method of the present invention are also given in the applicant's co-pending applications GB 9824818.0 and EP 0764290, where it will be appreciated that the colorants of Formula (1) herein replace some or all of the colorants used in these prior art formulations.

30 Preferably the ink of the present invention comprises from about 10 to about 99.6, preferably from about 30 to about 99.5, more preferably from about 50 to about 99, parts of the liquid medium; and from about 90 to about 0.4 parts, preferably from about 70 to about 0.5, more preferably from about 50 to about 1, parts of the other ingredients; where all parts are by weight and the number of parts totals 100.

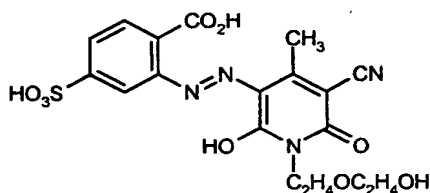
35 The inks according to a further aspect of the invention may be prepared by mixing the ingredients in any order. Suitable mixing techniques are well known in the art, for example agitation, ultrasonication or stirring of the components. The ingredients may be present in the ink in any form suitable for application to the substrate, for example the form of a dispersion, emulsification, suspension, solution or a combination thereof.

Examples of further media for inks of the present invention comprising a mixture of water and one or more organic solvents are described in US 4,963,189, US 4,703,113, US 4,626,284 and EP 0425150-A.

Dyes of the invention will now be illustrated by the following examples in which all parts and percentages are by weight unless specified otherwise. In the Examples (and previously), compounds referred to by reference to CI numbers are the dyestuffs identified by these numbers in the Colour Index International, 3rd Edition, 3rd Revision. In each of the following Examples, the inks were tested and the results were set out in tables.

Example 1

Preparation of:



Stage 1(a)

Preparation of the pyridone coupler: 1-(2'-hydroxyethoxyethyl)-3-cyano-4-methyl-6-hydroxy-2-pyridone

Ethylcyanoacetate (115 parts) was slowly added to 2-(2-aminoethoxy)ethanol (134 parts) with stirring, while maintaining the temperature below 30°C. On completion of the addition, the mixture was heated at 95°C for 3 hours then cooled back to room temperature. Methyl acetoacetate (123 parts) was added, maintaining the temperature below 30°C, the whole mixture was then cooled to <10°C before adding ethylamine (57.6 parts). The resultant mixture was heated at 90°C for 18 hours, then cooled to room temperature. On acidification to pH1 with concentrated hydrochloric acid, the product precipitated out. This was isolated by filtering, washing with a small amount of 2N HCl and finally drying at 60°C to yield 81 parts of the above pyridone coupler.

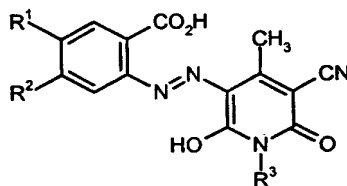
Stage 1(b)

Preparation of title compound

2-Amino-4-sulphobenzoic acid (27.2 parts) was stirred in water (200 parts) at pH5 until dissolved. The solution was cooled to <10°C and concentrated HCl (47 parts) was added. Sodium nitrite (6.8 parts) was slowly added and the reaction mixture was stirred at 0-10°C for 30 minutes. Excess nitrous acid was then removed by addition of sulphamic acid, until the diazo mixture was negative to starch-iodide. To this was added a solution

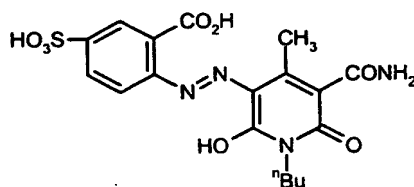
of the pyridone coupler (53 parts) from Stage 1 (a) in water (200 parts), which had been adjusted to pH8 with 2N NaOH. The temperature of the reaction mixture was maintained below 10°C during the addition. The mixture was then stirred for 16 hours whilst warming to room temperature. The dark yellow solution was acidified to pH 1 with concentrated HCl and the resultant precipitate was collected by filtration. The precipitate was re-dissolved in water (200 parts), and adjusted to pH9 with 0.88 S.G. ammonia. The product was then re-precipitated by pouring on to concentrated HCl (35 parts) and collected by filtration. The product was dissolved in ammonia and re-precipitated and collected by filtration once more. Finally the product was dissolved in water (200 parts) containing ammonia at pH9, dialysed to remove the inorganic components, screened through a 0.45 μ filter and dried at 60°C to yield the title compound as a yellow powder of its ammonium salt (7.7 parts).

The following dyes were made by an analogous method to that described in Example 1:



Ex	R ¹	R ²	R ³
2	H	SO ₃ H	ⁿ Bu
3	SO ₃ H	H	ⁿ Bu
4	H	SO ₃ H	2-Ethylhexyl
5	SO ₃ H	H	2-Ethylhexyl
6	H	SO ₃ H	C ₂ H ₄ OH
7	H	SO ₃ H	C ₂ H ₄ NH ₂
8	H	SO ₃ H	CH ₂ C(CH ₃) ₃
9	H	SO ₃ H	C ₂ H ₄ Oet
10	H	SO ₃ H	Cyclohexyl
11	H	SO ₃ H	n-Hexyl
12	H	SO ₃ H	C ₃ H ₆ Oet
13	H	SO ₃ H	C ₅ H ₁₀ OH
14	SO ₃ H	H	C ₂ H ₄ OC ₂ H ₄ OH
15	SO ₃ H	H	C ₃ H ₆ OH
16	SO ₃ H	H	C ₂ H ₄ Oet

Example 17
Preparation of



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Stage 17(a)

Preparation of the pyridone coupler: 1-n-butyl-3-carbonamido-4-methyl-6-hydroxy-2-pyridone

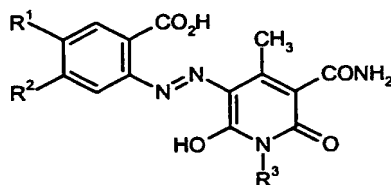
10 1-n-Butyl-3-cyano-4-methyl-6-hydroxy-2-pyridone (103 parts) was added carefully to 1.84 S.G. sulphuric acid (370 parts), maintaining the temperature below 50°C. After the addition was complete the temperature was raised to 75°C for 12 hours. The reaction mixture was allowed to cool to room temperature, then drowned out onto ice (400 parts). The solution was carefully neutralised with calcium carbonate and screened; the solids were further washed through with copious amounts of water and ethanol. Finally, the solution was evaporated to dryness under reduced pressure and the solids dried at 60°C to give the above pyridone coupler as a light grey powder (122 parts).

Stage 17(b)

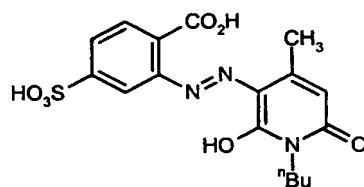
Preparation of title compound

20 The title compound was made in an analogous manner to the dyestuff in Example 1, substituting a molar equivalent of the pyridone coupler from Stage 17(a) for the coupler used in Example 1 Stage 1(b), and a molar equivalent of 2-amino-5-sulphobenzoic acid for the diazo component used in Example 1 Stage 1(b).

25 The following dyes were made by an analogous method to that described in Example 17:



Ex	R ¹	R ²	R ³
18	SO ₃ H	H	C ₂ H ₅
19	SO ₃ H	H	2-Ethylhexyl
20	SO ₃ H	H	ⁿ Pr
21	H	SO ₃ H	ⁿ Pr
22	H	SO ₃ H	ⁿ Bu

Example 23**Preparation of**

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Stage 23(a)**Preparation of the pyridone coupler: 1-(ⁿbutyl)-4-methyl-6-hydroxy-2-pyridone**

1-(ⁿButyl)-3-cyano-4-methyl-6-hydroxy-2-pyridone (20.6 parts) was added slowly to 75% sulphuric acid (40.6 parts). After addition the solution was heated at 125°C for 3 hours then cooled back to room temperature. The thick oil was poured onto ice (200 parts) with good stirring. 47% Sodium hydroxide solution was then carefully added until the product started to solidify. After stirring for a further 30 minutes, the solid was collected by filtration and dried at 60°C to yield the title pyridone coupler as a brown powder (17.5 parts).

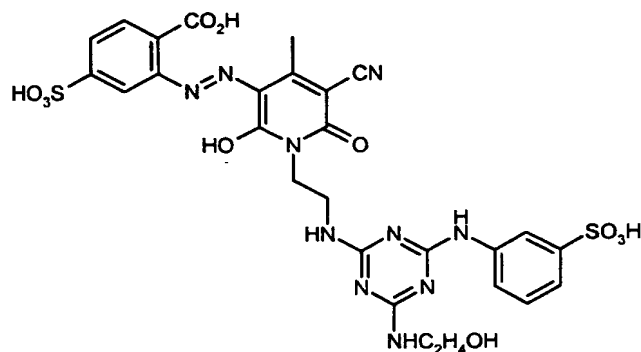
15

Stage 23(b)**Preparation of title compound**

The title compound was made in an analogous manner to the dyestuff in Example 1, substituting a molar equivalent of the pyridone coupler from Stage 23(a) for the coupler used in Example 1 Stage 1(b).

20

25

Example 24Preparation of

5

Stage 24(a)Preparation of the pyridone coupler: 1-(2'-aminoethyl)-3-cyano-4-methyl-6-hydroxy-2-pyridone

10 This coupler was made in an analogous manner to that described in Example 1 Stage 1(a), substituting ethylene diamine (5 times molar excess) for the 2-(2-aminoethoxy)ethanol.

Stage 24(b)

15 Preparation of the intermediate: 5-(2'-carboxy-5'-sulphophenylazo)-1-(2'-aminoethyl)-3-cyano-4-methyl-6-hydroxy-2-pyridone

This intermediate was made in an analogous manner to the dyestuff in Example 1, substituting a molar equivalent of the pyridone coupler from Stage 24(a) for the coupler prepared in Example 1 Stage 1(a).

20 Stage 24(c)

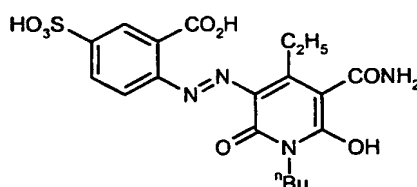
Preparation of the title compound

25 Cyanuric chloride (2.6 parts) was dissolved in acetone (20 parts) and poured onto ice/water (100 parts) at 0-5°C. A solution of metanilic acid (2.4 parts) in water (50 parts) at pH7 was then added to the cyanuric chloride suspension, maintaining the reaction at 0-5°C and pH6. The mixture was stirred under these conditions for 2 hours. To this was then added a solution of 5-(2'-carboxy-5'-sulphophenylazo)-1-(2'-aminoethyl)-3-cyano-4-methyl-6-hydroxy-2-pyridone (5.2 parts) prepared as described in Stage 24(b), in water (100 parts) at pH8.5, the mixture being stirred at pH8.5, 45°C for 12 hours. After cooling to room temperature the solution was acidified to pH 1 with concentrated HCl, and the solid was collected by filtration, dialysed and dried. This intermediate (8.7 parts) was then re-dissolved in water (400 parts) and ethanolamine (4.6 parts) was added. The solution

30

was then heated at 70°C for 6 hours. After cooling to room temperature, the product was precipitated by acidifying to pH 1 with concentrated HCl and was collected by filtration. It was then re-dissolved in water (200 parts), adjusted to pH9 with 0.88S.G. ammonia and re-precipitated by pouring on to concentrated HCl (35 parts). After stirring for 10 minutes the product was collected by filtration then re-dissolved in ammonia and re-precipitated with concentrated HCl once more. After collection by filtration, the product was dialysed, screened through a 0.45 μ filter and dried at 60°C to yield the ammonium salt of the title dye as a yellow powder (3.3 parts).

10 Example 25
Preparation of



15 Stage 25(a)
Preparation of the intermediate pyridone coupler; 1-nbutyl-3-cyano-4-ethyl-6-hydroxy-2-pyridone

Ethylcyanoacetate (57 parts) was slowly added to n-butylamine (40 parts) with stirring, while maintaining the temperature below 30°C. On completion of the addition, the mixture was heated at 95°C for 3 hours then cooled back to room temperature. Methyl propionylacetate (65 parts) was then added followed by ethylamine (29 parts), maintaining the temperature below 30°C the whole time. The resultant mixture was heated at 90°C for 18 hours, then cooled to room temperature. The solution was poured slowly on to ice (400 parts) and adjusted to pH1 with concentrated hydrochloric acid to produce a sticky solid. The supernatant liquid was decanted off and the solid dried under vacuum to yield 80 parts of the above intermediate

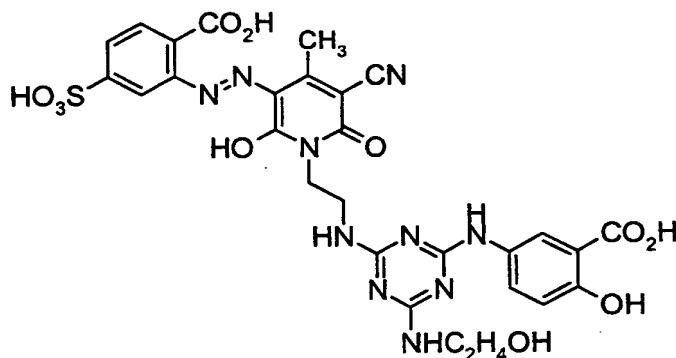
Stage 25(b)
Preparation of the pyridone coupler; 1-nbutyl-3-cyanamido-4-ethyl-6-hydroxy-2-pyridone

The intermediate coupler (66 parts) from Stage 25 (a) was added slowly to 1.84 S.G. sulphuric acid (220 parts), maintaining the temperature below 50°C. After the addition was complete, the temperature was raised to 70°C for 8 hours. The reaction mixture was allowed to cool to room temperature, then drowned out into an ice/water mixture with vigorous stirring. The solid which precipitated out was isolated by filtration and dried at 60°C to yield the above coupler as an off-white powder (91 parts).

Stage 25(c)Preparation of title compound

The title compound was made in an analogous manner to the dyestuff in Example 1, substituting a molar equivalent of the pyridone coupler from Stage 25(b) for the coupler prepared in Example 1 Stage 1(a), and a molar equivalent of 2-amino-5-sulphobenzoic acid for the diazo component used in Example 1 Stage 1 (b).

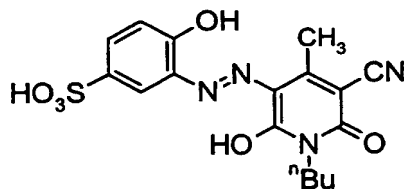
For the purpose of evaluating the spectra and resistance properties of formulations containing the dyes, the inks were bar-coated on to microscope slides using a No.1 K-bar (RK Print-Coat Instruments Ltd.), and the slides cured at 200°C for 15 minutes. The resultant films had a thickness of approximately 2µm.

Example 26

Example 26 was prepared as in Example 24 except that in Stage 24 (c) 5-aminosalicylic acid was used in place of metanilic acid

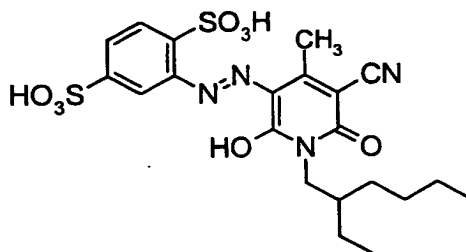
Comparative Dye A

Comparative dye A was prepared as in Stage 1(b) except that 2-aminophenol-4-sulphonic acid was reacted with 1-n-butyl-3-cyano-4-methyl-6-hydroxy-2-pyridone.

Comparative Dye B

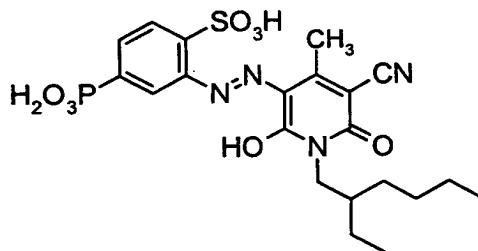
Comparative dye B was prepared by forming a pyridone coupler as in Stage 1 (a) except that 2-ethylhexylamine was used in place of 2-(2-aminoethoxy)ethanol and then

preparing the compound as in Stage 1(b) except that aniline-2,5-disulphonic acid was used in place of 2-amino-4-sulphobenzoic acid.



5 Comparative Dye C

Comparative dye C was prepared using the coupler as prepared as comparative dye B but using 3-amino-4-sulphophenyl phosphonic acid in place of 2-ethylhexylamine in Stage 1(b).

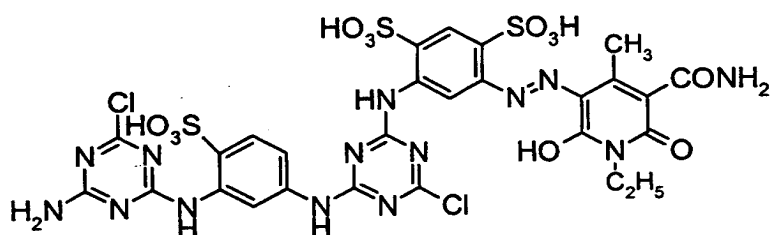


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Comparative Dye D

Comparative dye D was prepared as in Example 6 of WO9829513.

15



Examples 26 to 46 and Comparative Examples 1 and 2

Inks with the following formulation were made (all parts by weight) :

20	Acrylic co-polymer (54% methyl methacrylate; 46% methacrylic acid)	13.2 parts
	Primid XL552 - ex EMS Chemie	4.4 parts
	2-Amino-2-methyl-1-propanol	13.2 parts
	Dye	3.0 parts
	Ammonium dodecylbenzenesulphonate	0.9 parts

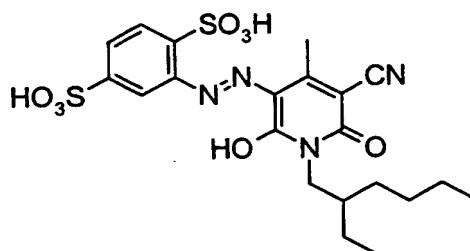
Water

65.3 parts

- 5 The inks gave very bright yellow films with high transmission at 520nm and low transmission at 420nm. Transmission was determined by measuring the spectra of the coloured films against a blank glass reference using a Minolta CM-3600d spectrophotometer. Light fastness properties were measured using a xenon lamp in an Atlas weatherometer Ci35A (lamp power 0.80 Wm^{-2} at 420nm, black panel 63°C , wet bulb depression 16°C), and the ΔE values were determined using a Minolta CM-3600d spectrophotometer. The transmission and light fastness results are tabulated below.

Ink Ex	Dye	%T @ 420nm	%T @ 520nm	LF - $\Delta E/100 \text{ hours}^1$
26	1	2	94	24.8
27	2	0	93	20.1
28	3	1	94	44.2
29	4	4	93	45.8
30	6	1	90	42.6
31	9	0	90	28.5
32	11	0	93	45.3
33	12	1	95	30.2
34	13	4	96	30.0
35	14	0	89	41.2
36	15	1	95	36.1
37	16	3	95	20.1
38	17	0	97	35.2
39	18	2	98	30.9
40	19	1	98	33.4
41	20	0	98	40.9
42	21	2	99	48.5
43	22	0	98	30.1
44	23	0	98	43.8
45	24	7	87	28.6
46	25	0	99	33.8
Comp. 1	A	14	65	77.3
Comp. 2	B	4	95	57.6

1.

Example 47 and Comparative Example 3

Inks with the following formulation were made (all parts by weight) :

5	Acrylic co-polymer (34% methyl methacrylate; 46% methacrylic acid 20% hydroxyethyl methacrylate)	12.3 parts
	Primid XL552 - ex EMS Chemie	4.1 parts
	0.88 S.G. ammonia	12.3 parts
	C.I. Reactive Blue 14	1.9 parts
10	Pyridone dye	3.3 parts
	Ammonium dodecylbenzenesulphonate	0.4 parts
	Triethyleneglycol monobutyl ether	0.9 parts
	Water	64.8 parts

15 The inks produced bright green highly transparent films, but the one made using a dye of this invention had far superior light fastness :

Example	Pyridone dye	LF = $\Delta E/100$ hrs
47	4	10.6
Comp 3	C	62.4

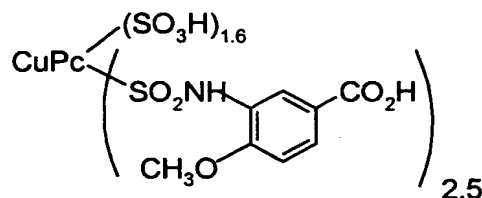
Examples 48 to 53

20 Inks similar to that used in Example 47 were made, using an alternative cyan component (all parts by weight) :

	Acrylic co-polymer (34% methylmethacrylate; 46% methacrylic acid 20% hydroxyethyl methacrylate)	11.5 parts
	Primid XL552 - ex EMS Chemie	3.9 parts
	0.88 S.G. ammonia	11.5 parts
25	Cyan D ¹	See Table
	Pyridone dye of the present invention	See Table
	Ammonium dodecylbenzenesulphonate	0.4 parts
	Triethyleneglycol monobutyl ether	2.9 parts
	Water	to 100 parts

All the inks produced bright green highly transparent films, but the ones made using dyes of this invention had far superior light fastness :

The cyan dye D had the following structure



5

Chromaticity (Y) values were measured on a Minolta CM-3600d spectrophotometer using a-C light source and 2° observer.

Example	Dye (%w/w)	Cyan D (% w/w)	Y	x	y	%T @ 540nm	LF = ΔE /100 hrs
48	1 (2.3)	2.5	59.7	0.315	0.557	84	13.8
49	2 (2.5)	3.0	59.1	0.311	0.560	83	16.9
50	9 (2.0)	2.5	59.1	0.306	0.550	83	15.1
51	17 (3.0)	2.0	55.0	0.287	0.578	80	13.3
52	23 (4.5)	1.5	55.2	0.301	0.571	78	14.0
53	26 (2.9)	2.0	51.0	0.319	0.570	76	11.2
Comp. 4	E (4.5)	1.5	58.6	0.298	0.560	83	42.3

10

Example 54

A photocurable ink was produced by mixing together NeoRad™ R-441 (50 parts; 33% solids UV-curable resin commercially available from Avecia Ltd.), NeoCryl™ BT-175 (5 parts; 40% solids acrylic resin commercially available from Avecia Ltd.), 0.88 S.G. ammonia (2 parts), CGI 1700 (1 part; photoinitiator commercially available from Ciba), azopyridone dye of Example 3 (5 parts) and water (37 parts). The ink was applied to a glass substrate by bar-coating and exposed to UV-light through a photomask. The unexposed portions of the film were then removed using a 1% sodium carbonate solution at 25°C and the remaining resin thermally cured at 150°C for 30 minutes to produce a bright yellow patterned film.

15

20

Example 55

To an ink base comprising 90 parts water and 10 parts 2-pyrrolidone was added the dye of Example 2 to give a 4% solution of the dye in the ink base. The solution was then adjusted to pH 10 using sodium hydroxide and filtered through a 0.45μ membrane.

25

When this was applied to paper using an ink-jet printer, strong bright yellow prints were obtained with excellent fastness properties.

Further inks for Colour Filters

Further inks which are suitable for making colour filters may be prepared having the formulations described in Tables I to VII below where the numbers denote parts by weight of each ingredient in the formulation. The compounds used may be in their free acid form and/or in the form of any effective salt. The number in the column headed compound is an example number of a dye of the invention described herein with the number in brackets being the amount used (w/w). The following abbreviations are also used in the tables:

- DB199 = Direct Blue 199 DB86 = Direct Blue 86 DB87 = Direct Blue 87
 AB9 = Acid Blue 9 RB15 = Reactive Blue 15 CD = cyan D as given herein
 PAA = Poly(acrylic acid) of M_w 2000 X = Primid XL552
 TEA = Triethanolamine TMP = Trimethylolpropane W= Water
 NMP = N-methyl-2-pyrrolidone 2P = 2-pyrrolidone
 BE = Butoxyethanol DEG = Diethylene glycol GBL = γ -butyrolactone
 ADBS = Ammonium dodecylbenzene sulphonate
 SDBS = Sodium dodecylbenzene sulphonate
 SURF = Surfynol 465 (Non-ionic surfactant available from Air Products)
 AMP = 2-Amino-2-methyl-1-propanol AM = Ammonia (0.88 S.G.)
 HT = 4-Hydroxy-TEMPO; and
 HMBS = 2-Hydroxy-4-methoxy-5-sulfobenzophenone.

TABLE I

Compound	DB199	DB86	PAA	X	W	BE	ADBS	AMP	AM
1(0.5)	3		15	5.5	60		1	15	
2(0.25)		3.	12	4	69.2 5	5	0.5		6
12(1)	3		12	6	62	5	1		10
4(0.2)	2		4	1	88.8		1	3	
5(0.5)		4	10	2	74.5	2			7
14(0.3)	3.5		12.5	4	61.4	5	0.8	12.5	
7(1)		1.5	8	2	80.5	2		5	
8(0.1)	2	0.9	11.5	6.5	63	5			11
6(3)		0.5	13.7	4.3	63.8		0.7	14	
10 (0.2)	2.8		15	5	61		1		15

TABLE II

Compound	DB199	PAA	X	TEA	TMP	W	2P	ADBS	AM
17(0.5)	4	14	5			61.5		1	14
22(0.5)	4	10.5	2.5			70	4	0.5	8
15(0.25)	3.5	15		5		60.5		0.75	15
24(0.1)	2.9	12			3	67	5		10
13(2)	0.5	12	2		2	76		0.5	5
11(0.1)	0.9	8	5			81	1		4
16(0.1)	3	15		5		63		0.9	13

TABLE III

Compound	DB199	PAA	TMP	W	2P	DEG	GBL	SURF	SDBS	AMP
18(0.5)	4	16	4	54.5			5	1		15
E(2.9)	0.1	12	3	71.2					0.8	10
19(3)	2	14	7	49	5	5				15
20(0.1)	1	4	1	87.4	0.5		1.5	0.5		4
20(0.5)	1.5	8	3	80.5		2			0.5	4

5

TABLE IV

Compound	AB9	CD	PAA	X	W	DEG	SURF	AMP	AM
19(3)	2		10	5	69		1		10
25(3)	1.5		14.5	5	62.5	3	0.5	10	
21(1)		4	18	7	50	5		15	
22(3)	1	1	12	4	64.5	2	0.5		12
8(2.5)		2.5	15	7.5	56.5		1	15	
18(1)			10	5	74.2		0.8		7
10(2)	2		10	3.5	67.5	5			10
11(2)		4	15	5	63.3		0.7	10	

TABLE V

Compound	AB9	RB15	PAA	X	W	BE	GBL	SURF	SDBS	AM
12(5)	2		13	4	55. 2	5			0.8	15
13(3)		2	15	5	59		5		1	10
23(1)		2	8	4	74. 5	2.5	2.5	0.5		5
6(0.5)	2		10	3	69. 5	4		0.5	0.5	10
16(2)		2	15	7.5	52. 5				1	20

TABLE VI

Compound	DB87	RB15	PAA	X	W	HT	HMSB	ADBS	AM
17(0.25)	3.5		13.5	4	63.5	1.75		0.5	14
18(0.1)		2.9	15	5	60	1		1	15
E (0.5)	3.5	0.5	12	6	65.5				12
1(0.25)	4.75	0.25	12	5	66.9			0.85	10
2(2)		0.5	12.5	4	68		1		12
3(1)		1.5	15	4.5	65.5	1	0.5	1	10
4(0.3)	3		12	4	67.8			0.9	12

5

TABLE VII

Compound	CD	PAA	X	TEA	W	HT	HMS B	NMP	BE	ADBS	AM
21(1)	3	15	5		53.5	2		5		0.5	15
21(2)	3	12		5	64	1	1		2		10
3(0.5)	4.5	12	2	2	64		2.5	2	2	0.5	8
4(0.2)	2.3	13	4.5		63.5	1.5				1	14

Further Inks for Ink Jet Printing

The inks described in Tables VIII and IX may be prepared wherein the compound described in the first column is the compound made in the above example of the same number. Numbers quoted in the second column onwards refer to the number of parts of the relevant ingredient and all parts are by weight. The inks may be applied to paper by thermal or piezo ink jet printing.

The following abbreviations are used in Table I and II:

PG = propylene glycol

DEG = diethylene glycol

NMP = N-methyl pyrrolidone

DMK = dimethylketone

5 IPA = isopropanol

MEOH = methanol

2P = 2-pyrrolidone

MIBK = methylisobutyl ketone

P12 = propane-1,2-diol

10 BDL = butane-2,3-diol

CET= cetyl ammonium bromide

PHO = Na_2HPO_4 and

TBT = tertiary butanol

TDG = thiodiglycol

TABLE VIII

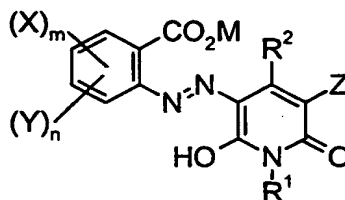
Example	Dye Content	Water	PG	DEG	NMP	DMK	NaOH	Na stearate	IPA	MEOH	2P	MIBK
1	2.0	80	5		6	4					5	
2	3.0	90		5	5		0.2			5	1	
2	10.0	85	3	8	3							1
3	2.1	91							4			5
4	3.1	86	5					0.2				
5	1.1	81			9		0.5				9	
6	2.5	60	4	15	3	3			6	10	5	4
7	5	65		20					10			
8	2.4	75	5	4		5				6		5
9	4.1	80	3	5	2	10		0.3				
10	3.2	65		5	4	6			5	4	6	5
11	5.1	96								4		
12	10.8	90	5						5			
13	10.0	80	2	6	2	5			1		4	
14	1.8	80		5							15	
15	2.6	84			11						5	
16	3.3	80	2			10				2		6
17	12.0	90				7	0.3		3			
18	5.4	69	2	20	2	1					3	3
19	6.0	91			4						5	

TABLE IX

Example	Dye Content	Water	PG	DEG	NMP	CET	TBT	TDG	BDL	PHO	2P	PI2
1	3.0	80	15			0.2					5	
20	9.0	90		5						1.2	5	
22	1.5	85	5	5		0.15	5.0	0.2		0.12		
23	2.5	90		6	4							
24	3.1	82	4	8		0.3					6	
25	0.9	85		10					5	0.2		
26	8.0	90		5	5			0.3				
1	4.0	70		10	4				1		4	11
1	2.2	75	4	10	3				2		6	
1	10.0	91			6						3	
1	9.0	76		9	7		3.0			0.95	5	
1	5.0	78	5	11							6	
2	5.4	86			7						7	
1	2.1	70	5	5	5	0.1	0.2	0.1	5	0.1	5	
26	2.0	90		10								
1	2	88						10				
2	5	78			5			12			5	
1	8	70	2		8			15			5	
1	10	80						8			12	
	10	80		10								

CLAIMS

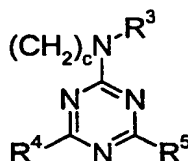
1. A compound of Formula (1)



Formula (1)

in which:

R¹ represents H, an optionally substituted C₁₋₈carbyl derived group, or a group of Formula A:



Formula A

where:

c is from 2 to 6;

R³ represents H or optionally substituted C₁₋₈carbyl derived group;

R⁴ and R⁵ independently represent an optional substituent;

R² represents an optionally substituted C₁₋₈carbyl derived group;

X, Y and Z independently represent H or an optional substituent group;

M represents H or a cation; and

m and n independently represent 0, 1 or 2;

with the provisos that:

at least one of R¹, R², X, Y or Z comprises a group of Formula SO₃M or PO₃M₂

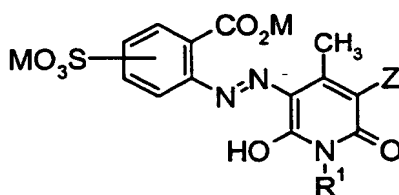
where M is independently as represented herein;

when n is 0; m is 1; X is a sulpho group para to the azo group; Z is H and R² is methyl then R¹ is other than ethyl

and the compound of Formula (1) is other than a compound of Formula II, III or IV as described herein.

2. A compound according to claim 1 wherein R¹ is of Formula A.

3. A compound according to claim 1 or claim 2 of Formula (2):



Formula (2)

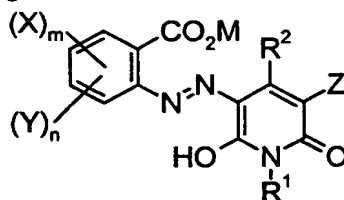
in which:

Z is CONH_2 , CN or H ;

5 R^1 is optionally substituted C_{2-8} alkyl or a glycol group;

with the proviso that if the SO_3M group is in the 4-position of the benzene ring then either R^1 is other than ethyl or Z is other than H .

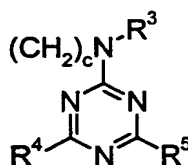
4. A composition comprising a solvent and at least one compound of Formula (1)



Formula (1)

in which:

R^1 represents H , an optionally substituted C_{1-8} carbonyl derived group, or a group of Formula A:



Formula A

where:

c is from 2 to 6;

R^3 represents H or optionally substituted C_{1-8} carbonyl derived group;

20 R^4 and R^5 independently represent an optional substituent;

R^2 represents an optionally substituted C_{1-8} carbonyl derived group;

X , Y and Z independently represent H or an optional substituent group;

M represents H or a cation; and

m and n independently represent 0, 1 or 2.

5. A composition comprising a solvent and at least one compound according to any one of claims 1 to 3.

6. A composition according to claim 4 or 5 which is an ink comprising
 (a) from 0.01 to 30 parts of a compound of Formula (1) according to claim 1; and
 (b) from 70 to 99.99 parts of a liquid medium or a low melting point solid medium:
 wherein all parts are by weight and the number of parts of (a) + (b)=100.

5

7. A composition according to claim 4 or 5 wherein the solvent comprises water and one or more water soluble organic solvent(s).

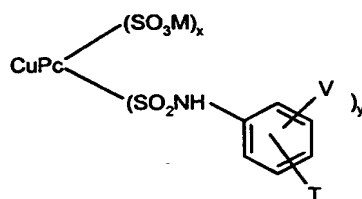
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8. A composition according to any one of claims 4 to 8 which comprises at least one further colorant.

15

9. A composition according to claim 8, where the further colorant(s) is selected from at least one cyan, green, red, magenta and/or orange colorant which is a dye or a pigment.

10. A composition according to claim 9, where the further colorant is a cyan dye of Formula (3)



Formula (3)

20

in which:

T represents H or an optional substituent;

V represents CO_2M , SO_3M or PO_3M_2 ;

M represents H or a cation;

x and y independently represent from 0 to 4; and

25

x + y is from 3 to 5.

11. A composition according to either claim 8 or claim 9, where the further colorant is selected from C.I. Pigment Green 7 and C.I. Pigment Green 36.

30

12. A composition according to any of claims 4 to 11 which is a green, red or yellow ink suitable for use in any of the process claimed in claims 13 to 17.

13. A process for preparing a patterned, cross-linked, polymer, film coating on a substrate comprising the steps of

35

- (a) applying to the substrate simultaneously and/or sequentially in any order:

- (i) one or more cross-linkable polymer precursor(s);
- (ii) optionally one or more additional cross-linker(s) capable of cross-linking the precursor(s) for the polymer(s); and
- (iii) one or more compound(s) of Formula (1) as described in claim 4 optionally with one or more other colorant(s);

(b) optionally patterning one or more non cross-linked film(s) of component (i); component (ii); component (iii) and/or mixture(s) thereof, optionally before application of further components; and

(c) initiating cross-linking the mixture of components (i), (ii) in situ, to form an optionally patterned, cross-linked polymeric film coating on the substrate.

14. A process according to claim 13, in which the process comprises a printing process.

15. A process according to claim 14, in which the printing process is an ink-jet printing process.

16. A process according to claim 14, in which the printing process comprises a photolithographic process.

17. A process according to claim 15, in which the polymer precursor(s) comprise water dissipatable polymer precursor(s).

18. A substrate obtainable by a process as claimed in any of claims 13 to 17.

19. A substrate according to claim 18, which comprises: a colour filter comprising a coloured, cross-linked, polymer coating on a transparent substrate; and/or a transparent, coloured, cross-linked, polymer coating on a substrate.

20. A substrate according to either claim 18 or 19, which has utility as a component for a coloured display.

21. A substrate according to any one of claims 18 to 20, which comprises an array of coloured trichromatic elements in which the trichromat is selected from: a red, green and blue trichromat; and a cyan, magenta and yellow trichromat.

22. A display which comprises a substrate according to any one of claims 18 to 21.

23. A display according to claim 22, which comprises a liquid crystal display.

24. A process for printing a substrate with a composition according to any of claims 4 to 12 using an ink-jet printer.
- 5 25. A cartridge suitable for use in an ink jet printer containing an ink according to any one of claims 4 to 12.
26. A paper, overhead projector slide, textile or colour filter printed with a composition according to any one of claims 4 to 12.
- 10 27. A colour filter comprising red, green and blue filter elements, or yellow, magenta and cyan filter elements, characterised in that the filter carries a compound of Formula (1) as defined in claim 4.

PATENT COOPERATION TREATY

PCT/ISA/220

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL SEARCH REPORT
OR THE DECLARATION

(PCT Rule 44.1)

To:

Intellectual Property Group
Attn. MAYALL, J.
AVECIA LIMITED
PO Box 42, Hexagon House
Manchester M9 8ZS
UNITED KINGDOM

Date of mailing
(day/month/year)

27/12/2000

Applicant's or agent's file reference

SMC 60384/WO

FOR FURTHER ACTION

See paragraphs 1 and 4 below

International application No.

PCT/GB 00/ 03550

International filing date
(day/month/year)

18/09/2000

Applicant

AVECIA LIMITED

1. ☒ The applicant is hereby notified that the International Search Report has been established and is transmitted herewith.

Filing of amendments and statement under Article 19:

The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

Where? Directly to the International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland
Facsimile No.: (41-22) 740.14.35

For more detailed instructions, see the notes on the accompanying sheet.

2. ☐ The applicant is hereby notified that no International Search Report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. ☐ **With regard to the protest** against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Further action(s):** The applicant is reminded of the following:

Shortly after **18 months** from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90*bis*.1 and 90*bis*.3, respectively, before the completion of the technical preparations for international publication.

Within **19 months** from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within **20 months** from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the International Searching Authority



European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Emmanuel Cherqui

These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions respectively.

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only.

What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

What documents must/may accompany the amendments?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

- (i) the claim is unchanged;
- (ii) the claim is cancelled;
- (iii) the claim is new;
- (iv) the claim replaces one or more claims as filed;
- (v) the claim is the result of the division of a claim as filed.

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."
2. [Where originally there were 15 claims and after amendment of all claims there are 11]:
"Claims 1 to 15 replaced by amended claims 1 to 11."
3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."
4. [Where various kinds of amendments are made]:
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

"Statement under article 19(1)" (Rule 46.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international application is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

Consequence if a demand for international preliminary examination has already been filed

If, at the time of filing any amendments under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the same time of filing the amendments with the International Bureau, also file a copy of such amendments with the International Preliminary Examining Authority (see Rule 62.2(a), first sentence).

Consequence with regard to translation of the international application for entry into the national phase

The applicant's attention is drawn to the fact that, where upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see Volume II of the PCT Applicant's Guide.

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference SMC 60384/W0	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/GB 00/ 03550	International filing date (day/month/year) 18/09/2000	(Earliest) Priority Date (day/month/year) 20/09/1999
Applicant AVECIA LIMITED		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☐ the text is approved as submitted by the applicant.

☒ the text has been established by this Authority to read as follows:

✓ **MONOAZO DYESTUFFS USEFUL FOR COLOUR FILTERS AND INK JET PRINTING**

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No. _____

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☐ None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No

P B 00/03550

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09B29/42 C09D11/00 G03F7/00 G02F1/1335

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09B C09D G03F G02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>EP 0 169 457 A (HOECHST AG) 29 January 1986 (1986-01-29) cited in the application examples 3,20 page 1, line 20 -page 4, line 16 page 5, formula (4c)</p> <p style="text-align: center;">--- -/--</p>	1,4,5



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

° Special categories of cited documents :

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document, but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

13 December 2000

Date of mailing of the international search report

27/12/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Ketterer, M

INTERNATIONAL SEARCH REPORT

International Application No

P B 00/03550

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Week 9004 Derwent Publications Ltd., London, GB; AN 1990-025870'04! XP002155449 H. YUTAKA: "color filter" & JP 01 303407 A (NIPPON KAYAKU CO. LTD.) cited in the application abstract & JP 01 303407 A (NIPPON KAYAKU CO. LTD.) 7 December 1989 (1989-12-07) page 35, left col., formula 1.</p> <p>---</p>	1
A	<p>PATENT ABSTRACTS OF JAPAN vol. 014, no. 406 (C-0754), 4 September 1990 (1990-09-04) & JP 02 153977 A (MITSUBISHI KASEI CORP), 13 June 1990 (1990-06-13) cited in the application abstract</p> <p>---</p>	1,4,5,24
A	<p>GB 1 359 171 A (CIBA GEIGY AG) 10 July 1974 (1974-07-10) cited in the application examples</p> <p>---</p>	1,4,5
A	<p>EP 0 268 897 A (BASF AG) 1 June 1988 (1988-06-01) examples 106-212</p> <p>---</p>	1,4,5
A	<p>GB 1 271 226 A (ICI LTD.) 19 April 1972 (1972-04-19) cited in the application page 2, line 21 - line 52; claims 1,2,6</p> <p>---</p>	1,2,4,5
A	<p>US 3 926 944 A (BERRIE ALISTAIR HOWARD ET AL) 16 December 1975 (1975-12-16) column 4, line 23 - line 39</p> <p>---</p>	1,4,5
A	<p>DE 951 524 C (FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT) 31 October 1956 (1956-10-31) examples</p> <p>-----</p>	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

P B 00/03550

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0169457	A	29-01-1986	DE 3427188 A BR 8503494 A DE 3561743 D IN 164505 A IN 169337 A JP 1757096 C JP 4043114 B JP 61037848 A KR 9309243 B MX 13439 A MX 159995 A US 4659807 A	30-01-1986 15-04-1986 07-04-1988 01-04-1989 28-09-1991 23-04-1993 15-07-1992 22-02-1986 24-09-1993 01-05-1993 23-10-1989 21-04-1987
JP 1303407	A	07-12-1989	NONE	
JP 02153977	A	13-06-1990	JP 2701387 B	21-01-1998
GB 1359171	A	10-07-1974	BE 767179 A CA 965779 A CS 163250 B DE 2123061 A ES 391225 A FR 2091415 A NL 7106678 A US 4067864 A	16-11-1971 08-04-1975 29-08-1975 25-11-1971 01-05-1974 14-01-1972 17-11-1971 10-01-1978
EP 0268897	A	01-06-1988	DE 3639155 A DE 3709567 A JP 63135456 A	26-05-1988 06-10-1988 07-06-1988
GB 1271226	A	19-04-1972	CH 569767 A CH 598335 A CH 599314 A CH 569770 A CH 579622 A CH 539675 A CS 166751 B CS 166755 B CS 166756 B CS 166759 B CS 166760 B CS 166761 B CS 166762 B DE 1948354 A DE 1967137 B ES 371853 A ES 371854 A FR 2019491 A FR 2061420 A JP 50031565 B NL 6914471 A,B, SU 416955 A SU 420186 A SU 368758 A SU 420185 A	28-11-1975 28-04-1978 31-05-1978 28-11-1975 15-09-1976 31-07-1973 29-03-1976 29-03-1976 29-03-1976 29-03-1976 29-03-1976 29-03-1976 29-03-1976 23-04-1970 04-10-1979 16-11-1971 16-11-1971 03-07-1970 18-06-1971 13-10-1975 26-03-1970 25-02-1974 15-03-1974 26-01-1973 15-03-1974
US 3926944	A	16-12-1975	GB 1348641 A US 3936436 A	20-03-1974 03-02-1976

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

P 00/03550

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 951524	C	NONE	

PCT

FEE CALCULATION SHEET

Annex to the Request

For receiving Office use only

International application No.

Date stamp of the receiving Office

Applicant's or agent's
file reference

SMC 60384100

Applicant

Avecia Limited

CALCULATION OF PRESCRIBED FEES

1. TRANSMITTAL FEE 55.00 T

2. SEARCH FEE 605.00 S

International search to be carried out by EPO
(If two or more International Searching Authorities are competent in relation to the international application, indicate the name of the Authority which is chosen to carry out the international search.)

3. INTERNATIONAL FEE

Basic Fee

The international application contains 47 sheets.

first 30 sheets 264.00 b1

17 x 6 = 102.00 b2

remaining sheets additional amount

Add amounts entered at b1 and b2 and enter total at B 366.00 B

Designation Fees

The international application contains ALL designations.

8 x 56 = 448.00 D

number of designation fees payable (maximum 8) amount of designation fee

Add amounts entered at B and D and enter total at I 814.00 I

(Applicants from certain States are entitled to a reduction of 75% of the international fee. Where the applicant is (or all applicants are) so entitled, the total to be entered at I is 25% of the sum of the amounts entered at B and D.)

4. FEE FOR PRIORITY DOCUMENT (if applicable) 22.00 P

5. TOTAL FEES PAYABLE 1496.00

Add amounts entered at T, S, I and P, and enter total in the TOTAL box

TOTAL

☐ The designation fees are not paid at this time.

MODE OF PAYMENT

☒ authorization to charge
deposit account (see below)

☐ cheque

☐ postal money order

☐ bank draft

☐ cash

☐ revenue stamps

☐ coupons

☐ other (specify):

DEPOSIT ACCOUNT AUTHORIZATION (this mode of payment may not be available at all receiving Offices)

The RO/ CIB ☒ is hereby authorized to charge the total fees indicated above to my deposit account.

☒ (this check-box may be marked only if the conditions for deposit accounts of the receiving Office so permit) is hereby authorized to charge any deficiency or credit any overpayment in the total fees indicated above to my deposit account.

☒ is hereby authorized to charge the fee for preparation and transmittal of the priority document to the International Bureau of WIPO to my deposit account.

DC2944
Deposit Account No.

15 September
Date (day/month/year)

C. Terry
Signature

PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty ☐

For receiving Office use only

International Application No ☐

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference
(if desired) (12 characters maximum) SMC 60384/WO

Box No ☐ TITLE OF INVENTION

Compounds, Compositions and Use

Box No ☐ APPLICANT

Name and address: (Family name followed by given name; for a legal entity, full official designation) The address must include postal code and name of country The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below

Avecia Limited
Hexagon House
Blackley
Manchester M9 8ZS
United Kingdom

☐ This person is also inventor ☐

Telephone No ☐

0161 740 1460

Facsimile No ☐

0161 721 5801

Teleprinter No ☐

State (that is, country) of nationality:

GB

State (that is, country) of residence:

GB

This person is applicant for the purposes of:

☐ all designated States

☒ all designated States except the United States of America

☐ the United States of America only

☐ the States indicated in the Supplemental Box

Box No ☐ FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

Name and address: (Family name followed by given name; for a legal entity, full official designation) The address must include postal code and name of country The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below

TALLANT, Neil Anthony
PO Box 42, Hexagon House
Blackley
Manchester M9 8ZS
United Kingdom

This person is:

☐ applicant only

☒ applicant and inventor

☐ inventor only (If this check-box is marked, do not fill in below)

State (that is, country) of nationality:

GB

State (that is, country) of residence:

GB

This person is applicant for the purposes of:

☐ all designated States

☐ all designated States except the United States of America

☒ the United States of America only

☐ the States indicated in the Supplemental Box

☒ Further applicants and/or (further) inventors are indicated on a continuation sheet ☐

Box No ☐ AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:

☒ agent

☐ common representative

Name and address: (Family name followed by given name; for a legal entity, full official designation) The address must include postal code and name of country

MAYALL, John
Intellectual Property Group
Avecia Limited
PO Box 42, Hexagon House
Blackley
Manchester M9 8ZS
United Kingdom

Telephone No ☐

0161 721 1794

Facsimile No ☐

0161 721 5801

Teleprinter No ☐

☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent ☐

Continuation of Box No III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)	
<i>If none of the following sub-boxes is used, this sheet should not be included in the request</i>	
Name and address: <i>(Family name followed by given name; for a legal entity, full official designation)</i> The address must include postal code and name of country The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below MILLARD, Christine PO Box 42, Hexagon House Blackley Manchester M9 8ZS United Kingdom	This person is: <input type="checkbox"/> applicant only <input checked="" type="checkbox"/> applicant and inventor <input type="checkbox"/> inventor only <i>(If this check-box is marked, do not fill in below)</i>
State <i>(that is, country)</i> of nationality: GB	State <i>(that is, country)</i> of residence: GB
This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input checked="" type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box	
Name and address: <i>(Family name followed by given name; for a legal entity, full official designation)</i> The address must include postal code and name of country The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below	This person is: <input type="checkbox"/> applicant only <input type="checkbox"/> applicant and inventor <input type="checkbox"/> inventor only <i>(If this check-box is marked, do not fill in below)</i>
State <i>(that is, country)</i> of nationality:	State <i>(that is, country)</i> of residence:
This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box	
Name and address: <i>(Family name followed by given name; for a legal entity, full official designation)</i> The address must include postal code and name of country The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below	This person is: <input type="checkbox"/> applicant only <input type="checkbox"/> applicant and inventor <input type="checkbox"/> inventor only <i>(If this check-box is marked, do not fill in below)</i>
State <i>(that is, country)</i> of nationality:	State <i>(that is, country)</i> of residence:
This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box	
Name and address: <i>(Family name followed by given name; for a legal entity, full official designation)</i> The address must include postal code and name of country The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below	This person is: <input type="checkbox"/> applicant only <input type="checkbox"/> applicant and inventor <input type="checkbox"/> inventor only <i>(If this check-box is marked, do not fill in below)</i>
State <i>(that is, country)</i> of nationality:	State <i>(that is, country)</i> of residence:
This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box	
Name and address: <i>(Family name followed by given name; for a legal entity, full official designation)</i> The address must include postal code and name of country The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below	This person is: <input type="checkbox"/> applicant only <input type="checkbox"/> applicant and inventor <input type="checkbox"/> inventor only <i>(If this check-box is marked, do not fill in below)</i>
State <i>(that is, country)</i> of nationality:	State <i>(that is, country)</i> of residence:
This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box	
<input type="checkbox"/> Further applicants and/or (further) inventors are indicated on another continuation sheet	

Box No.V DESIGNATION OF STATES

The following designations are hereby made under Rule 4.9(a) (mark the applicable check-boxes, at least one must be marked):

Regional Patent

- ☒ **AP ARIPO Patent:** GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, MZ Mozambique, SD Sudan, SL Sierra Leone, SZ Swaziland, TZ United Republic of Tanzania, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- ☒ **EA Eurasian Patent:** AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- ☒ **EP European Patent:** AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- ☒ **OA OAPI Patent:** BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line)

National Patent (if other kind of protection or treatment desired, specify on dotted line):

- | | |
|-------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|
| <input checked="" type="checkbox"/> AE United Arab Emirates | <input checked="" type="checkbox"/> LC Saint Lucia |
| <input checked="" type="checkbox"/> AG Antigua and Barbuda | <input checked="" type="checkbox"/> LK Sri Lanka |
| <input checked="" type="checkbox"/> AL Albania | <input checked="" type="checkbox"/> LR Liberia |
| <input checked="" type="checkbox"/> AM Armenia | <input checked="" type="checkbox"/> LS Lesotho |
| <input checked="" type="checkbox"/> AT Austria | <input checked="" type="checkbox"/> LT Lithuania |
| <input checked="" type="checkbox"/> AU Australia | <input checked="" type="checkbox"/> LU Luxembourg |
| <input checked="" type="checkbox"/> AZ Azerbaijan | <input checked="" type="checkbox"/> LV Latvia |
| <input checked="" type="checkbox"/> BA Bosnia and Herzegovina | <input checked="" type="checkbox"/> MA Morocco |
| <input checked="" type="checkbox"/> BB Barbados | <input checked="" type="checkbox"/> MD Republic of Moldova |
| <input checked="" type="checkbox"/> BG Bulgaria | <input checked="" type="checkbox"/> MG Madagascar |
| <input checked="" type="checkbox"/> BR Brazil | <input checked="" type="checkbox"/> MK The former Yugoslav Republic of Macedonia |
| <input checked="" type="checkbox"/> BY Belarus | <input checked="" type="checkbox"/> MN Mongolia |
| <input checked="" type="checkbox"/> BZ Belize | <input checked="" type="checkbox"/> MW Malawi |
| <input checked="" type="checkbox"/> CA Canada | <input checked="" type="checkbox"/> MX Mexico |
| <input checked="" type="checkbox"/> CH and LI Switzerland and Liechtenstein | <input checked="" type="checkbox"/> MZ Mozambique |
| <input checked="" type="checkbox"/> CN China | <input checked="" type="checkbox"/> NO Norway |
| <input checked="" type="checkbox"/> CR Costa Rica | <input checked="" type="checkbox"/> NZ New Zealand |
| <input checked="" type="checkbox"/> CU Cuba | <input checked="" type="checkbox"/> PL Poland |
| <input checked="" type="checkbox"/> CZ Czech Republic | <input checked="" type="checkbox"/> PT Portugal |
| <input checked="" type="checkbox"/> DE Germany | <input checked="" type="checkbox"/> RO Romania |
| <input checked="" type="checkbox"/> DK Denmark | <input checked="" type="checkbox"/> RU Russian Federation |
| <input checked="" type="checkbox"/> DM Dominica | <input checked="" type="checkbox"/> SD Sudan |
| <input checked="" type="checkbox"/> DZ Algeria | <input checked="" type="checkbox"/> SE Sweden |
| <input checked="" type="checkbox"/> EE Estonia | <input checked="" type="checkbox"/> SG Singapore |
| <input checked="" type="checkbox"/> ES Spain | <input checked="" type="checkbox"/> SI Slovenia |
| <input checked="" type="checkbox"/> FI Finland | <input checked="" type="checkbox"/> SK Slovakia |
| <input checked="" type="checkbox"/> GB United Kingdom | <input checked="" type="checkbox"/> SL Sierra Leone |
| <input checked="" type="checkbox"/> GD Grenada | <input checked="" type="checkbox"/> TJ Tajikistan |
| <input checked="" type="checkbox"/> GE Georgia | <input checked="" type="checkbox"/> TM Turkmenistan |
| <input checked="" type="checkbox"/> GH Ghana | <input checked="" type="checkbox"/> TR Turkey |
| <input checked="" type="checkbox"/> GM Gambia | <input checked="" type="checkbox"/> TT Trinidad and Tobago |
| <input checked="" type="checkbox"/> HR Croatia | <input checked="" type="checkbox"/> TZ United Republic of Tanzania |
| <input checked="" type="checkbox"/> HU Hungary | <input checked="" type="checkbox"/> UA Ukraine |
| <input checked="" type="checkbox"/> ID Indonesia | <input checked="" type="checkbox"/> UG Uganda |
| <input checked="" type="checkbox"/> IL Israel | <input checked="" type="checkbox"/> US United States of America |
| <input checked="" type="checkbox"/> IN India | <input checked="" type="checkbox"/> UZ Uzbekistan |
| <input checked="" type="checkbox"/> IS Iceland | <input checked="" type="checkbox"/> VN Viet Nam |
| <input checked="" type="checkbox"/> JP Japan | <input checked="" type="checkbox"/> YU Yugoslavia |
| <input checked="" type="checkbox"/> KE Kenya | <input checked="" type="checkbox"/> ZA South Africa |
| <input checked="" type="checkbox"/> KG Kyrgyzstan | <input checked="" type="checkbox"/> ZW Zimbabwe |
| <input checked="" type="checkbox"/> KP Democratic People's Republic of Korea | |
| <input checked="" type="checkbox"/> KR Republic of Korea | |
| <input checked="" type="checkbox"/> KZ Kazakhstan | |

Check-box reserved for designating States which have become party to the PCT after issuance of this sheet:

☐

Precautionary Designation Statement: In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation (including fees) must reach the receiving Office within the 15-month time limit.)

Supplemental Box If the Supplemental Box is not used, this sheet should not be included in the request

1 If, in any of the Boxes, the space is insufficient to furnish all the information: in such case, write "Continuation of Box No []" [indicate the number of the Box] and furnish the information in the same manner as required according to the captions of the Box in which the space was insufficient, in particular:

- (i) if more than two persons are involved as applicants and/or inventors and no "continuation sheet" is available: in such case, write "Continuation of Box No []" and indicate for each additional person the same type of information as required in Box No [] The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below;
- (ii) if, in Box No [] or in any of the sub-boxes of Box No [], the indication "the States indicated in the Supplemental Box" is checked: in such case, write "Continuation of Box No []" or "Continuation of Boxes No [] and No []" (as the case may be), indicate the name of the applicant(s) involved and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is applicant;
- (iii) if, in Box No [] or in any of the sub-boxes of Box No [], the inventor or the inventor/applicant is not inventor for the purposes of all designated States or for the purposes of the United States of America: in such case, write "Continuation of Box No []" or "Continuation of Box No []" or "Continuation of Boxes No [] and No []" (as the case may be), indicate the name of the inventor(s) and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is inventor;
- (iv) if, in addition to the agent(s) indicated in Box No [], there are further agents: in such case, write "Continuation of Box No []" and indicate for each further agent the same type of information as required in Box No [];
- (v) if, in Box No [], the name of any State (or OAPI) is accompanied by the indication "patent of addition," or "certificate of addition," or if, in Box No [], the name of the United States of America is accompanied by an indication "continuation" or "continuation-in-part": in such case, write "Continuation of Box No []" and the name of each State involved (or OAPI), and after the name of each such State (or OAPI), the number of the parent title or parent application and the date of grant of the parent title or filing of the parent application;
- (vi) if, in Box No [], there are more than three earlier applications whose priority is claimed: in such case, write "Continuation of Box No []" and indicate for each additional earlier application the same type of information as required in Box No [];
- (vii) if, in Box No [], the earlier application is an ARIPO application: in such case, write "Continuation of Box No []", specify the number of the item corresponding to that earlier application and indicate at least one country party to the Paris Convention for the Protection of Industrial Property or one Member of the World Trade Organization for which that earlier application was filed


2 If, with regard to the precautionary designation statement contained in Box No [], the applicant wishes to exclude any State(s) from the scope of that statement: in such case, write "Designation(s) excluded from precautionary designation statement" and indicate the name or two-letter code of each State so excluded

3 If the applicant claims, in respect of any designated Office, the benefits of provisions of the national law concerning non-prejudicial disclosures or exceptions to lack of novelty: in such case, write "Statement concerning non-prejudicial disclosures or exceptions to lack of novelty" and furnish that statement below

Continuation of Box IV

FAWKES, David Melville
LOCKE, Timothy John
PUGSLEY, Roger Graham
REVELL, Christopher
SCHMITT, Maja
SHELLER, Alan

All of Intellectual Property Group, Avecia Limited, PO Box 42, Hexagon House, Blackley, Manchester M9 8ZS, United Kingdom

Box No VI PRIORITY CLAIM		<input type="checkbox"/> Further priority claim indicated in the Supplemental Box		
Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country	regional application: regional Office	international application: receiving Office
item (1) 20/09/1999 20 September 1999	9922136.8	GB		
item (2)				
item (3)				
<input checked="" type="checkbox"/> The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office) identified above as item(s): 1				
<small>* Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4(0)(b)(ii)) <input type="checkbox"/> See Supplemental Box</small>				
Box No VII INTERNATIONAL SEARCHING AUTHORITY				
Choice of International Searching Authority (ISA) <small>(if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):</small>		Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority):		
ISA / EPO		Date (day/month/year) Number Country (or regional Office)		
Box No VIII CHECK LIST; LANGUAGE OF FILING				
This international application contains the following number of sheets: request : 05 description (excluding sequence listing part) : 36 claims : 05 abstract : 01 drawings : sequence listing part of description : Total number of sheets : 47		This international application is accompanied by the item(s) marked below: 1 <input type="checkbox"/> fee calculation sheet 2 <input checked="" type="checkbox"/> separate signed power of attorney 3 <input type="checkbox"/> copy of general power of attorney; reference number, if any: 4 <input type="checkbox"/> statement explaining lack of signature 5 <input type="checkbox"/> priority document(s) identified in Box No VI as item(s): 6 <input type="checkbox"/> translation of international application into (language): 7 <input type="checkbox"/> separate indications concerning deposited microorganism or other biological material 8 <input type="checkbox"/> nucleotide and/or amino acid sequence listing in computer readable form 9 <input type="checkbox"/> other (specify):		
Figure of the drawings which should accompany the abstract:		Language of filing of the international application: ENGLISH		
Box No IX SIGNATURE OF APPLICANT OR AGENT				
Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request)				
For Avecia Limited - TALLANT, NA. and MILLARD, C.				
 MAYALL, John				

For receiving Office use only	
1 <input type="checkbox"/> Date of actual receipt of the purported international application: 3 <input type="checkbox"/> Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application: 4 <input type="checkbox"/> Date of timely receipt of the required corrections under PCT Article 11(2): 5 <input type="checkbox"/> International Searching Authority (if two or more are competent): ISA /	2 <input type="checkbox"/> Drawings: <input type="checkbox"/> received: <input type="checkbox"/> not received: 6 <input type="checkbox"/> Transmittal of search copy delayed until search fee is paid

For International Bureau use only
Date of receipt of the record copy by the International Bureau:

PATENT COOPERATION TREATY

REC'L 24 MAY 2002

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference SMC 60384/WO	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/GB00/03550	International filing date (day/month/year) 18/09/2000	Priority date (day/month/year) 20/09/1999
International Patent Classification (IPC) or national classification and IPC C09B29/42		
Applicant AVECIA LIMITED		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.


2. This REPORT consists of a total of 4 sheets, including this cover sheet.

- ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 6 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 20/03/2001	Date of completion of this report 22.05.2002
Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized officer Ketterer, M Telephone No. +31 70 340 3645



**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/GB00/03550

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

1-36 as originally filed

Claims, No.:

1-27 as received on 08/10/2001 with letter of 04/10/2001

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2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, _sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB00/03550

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	2-4,6-27
	No:	Claims	1,5
Inventive step (IS)	Yes:	Claims	2-4,6-27
	No:	Claims	1,5
Industrial applicability (IA)	Yes:	Claims	1-27
	No:	Claims	

2. Citations and explanations **see separate sheet**

V. Reference is made to the following document:

D1: EP -A- 0 169 457

V.1. D1 is novelty destroying for claims 1 and 5. Regarding formula (4c) on page 5 of D1, all compounds represented by this formula, in which M stands for substituents other than hydrogen (see D1, page 4, lines 11-13) and Y stands for the meanings given on page 3 of D1 are novelty destroying for claims 1 and 5 (water can be regarded as a solvent). Formula (4c) from page 5 of D1 is not completely disclaimed from claim 1.

V.2. Claims 2-4,6-27 seem to be new with regard to the disclosed prior art.

V.2.1. D1 does not disclose compounds with a triazin moiety falling under claim 2 of the application. D1 furthermore only discloses aqueous (free from organic solvents) solutions of reactive dyes.

The monoazo compounds of D1 are used as fibre reactive dyestuffs to dye cellulose fiber materials, such as cotton, as well as wool etc.

The subject matter of the current application relates to compounds, compositions, patterned substrates (such as displays and colour filters) comprising the compounds of current claim 1 and to methods of making the same.

The colour of the produced coloured patterns or images on substrates has to have high resistance (fastness) to light, water, heat and/or solvents in many areas of for instance the electronics and printing industries (colour filters [used for liquid crystal displays (LCDs) e.g. in flat screen displays, in small television receivers or portable computers etc.], in ink-jet printing, electrophoto-graphic imaging).

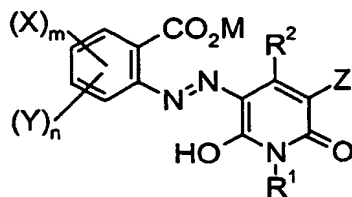
D1 therefore deals with a different technical field and a skilled person looking for coloured components for use in the electronics industry would not take D1 into consideration by searching such components.

Therefore, the new claims 2-4,6-27 are also inventive over D1.

V.3. The documents WO97/048117 as well as WO97/002955 are obviously not relevant in the context of the current application.

CLAIMS

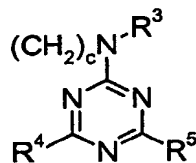
1. A compound of Formula (1)



Formula (1)

in which:

R¹ represents H, an optionally substituted C₁₋₈carbonyl derived group, or a group of Formula A:



Formula A

where:

c is from 2 to 6;

R³ represents H or optionally substituted C₁₋₈carbonyl derived group;

R⁴ and R⁵ independently represent an optional substituent;

R² represents an optionally substituted C₁₋₈carbonyl derived group;

X, Y and Z independently represent H or an optional substituent group;

M represents H or a cation; and

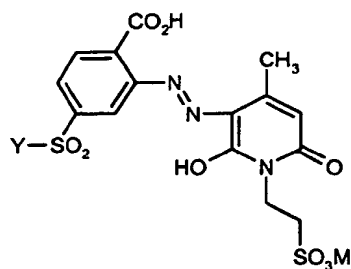
m and n independently represent 0, 1 or 2;

with the provisos that:

i) at least one of R¹, R², X, Y or Z comprises a group of Formula SO₃M or PO₃M₂ where M is independently as represented herein;

ii) when n is 0; m is 1; X is a sulpho group para to the azo group; Z is H and R² is methyl then R¹ is other than ethyl; and

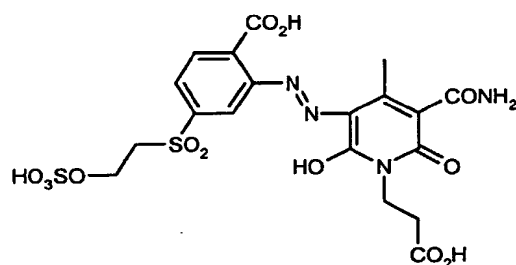
iii) the compound of Formula (1) is other than:



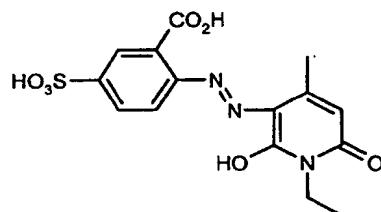
wherein:

Y is a vinyl group or an ethyl group which contains in the .beta.-position a substituent which is eliminatable as an anion under alkaline conditions; and

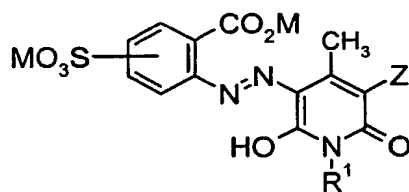
M is a hydrogen atom or one equivalent of a monovalent, divalent or trivalent metal: and



and



2. A compound according to claim 1 wherein R¹ is of Formula A.
3. A compound according to claim 1 or claim 2 of Formula (2):



Formula (2)

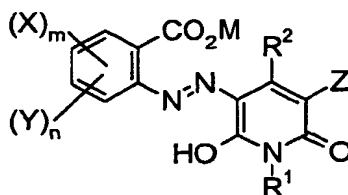
in which:

Z is CONH₂, CN or H;

R¹ is optionally substituted C₂₋₈alkyl or a glycol group;

with the proviso that if the SO₃M group is in the 4-position of the benzene ring then either R¹ is other than ethyl or Z is other than H.

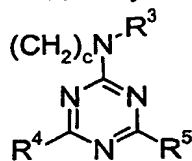
4. A composition comprising an organic solvent free from water or water and one or more water soluble organic solvent(s), and at least one compound of Formula (1)



Formula (1)

in which:

R¹ represents H, an optionally substituted C₁₋₈carbonyl derived group, or a group of Formula A:



Formula A

where:

c is from 2 to 6;

R³ represents H or optionally substituted C₁₋₈carbonyl derived group;

R⁴ and R⁵ independently represent an optional substituent;

R² represents an optionally substituted C₁₋₈carbonyl derived group;

X, Y and Z independently represent H or an optional substituent group;

M represents H or a cation; and

m and n independently represent 0, 1 or 2.

5. A composition comprising a solvent and at least one compound according to any one of claims 1 to 3.

6. A composition according to claim 4 or 5 which is an ink comprising
 (a) from 0.01 to 30 parts of a compound of Formula (1) according to claim 1; and
 (b) from 70 to 99.99 parts of a liquid medium or a low melting point solid medium:

(iii) one or more compound(s) of Formula (1) as described in claim 4 optionally with one or more other colorant(s);

(b) optionally patterning one or more non cross-linked film(s) of component (i); component (ii); component (iii) and/or mixture(s) thereof, optionally before application of further components; and

(c) initiating cross-linking the mixture of components (i), (ii) in situ, to form an optionally patterned, cross-linked polymeric film coating on the substrate.

14. A process according to claim 13, in which the process comprises a printing process.

15. A process according to claim 14, in which the printing process is an ink-jet printing process.

16. A process according to claim 14, in which the printing process comprises a photolithographic process.

17. A process according to claim 15, in which the polymer precursor(s) comprise water dissipatable polymer precursor(s).

18. A substrate obtainable by a process as claimed in any of claims 13 to 17.

19. A substrate according to claim 18, which comprises: a colour filter comprising a coloured, cross-linked, polymer coating on a transparent substrate; and/or a transparent, coloured, cross-linked, polymer coating on a substrate.

20. A substrate according to either claim 18 or 19, which has utility as a component for a coloured display.

21. A substrate according to any one of claims 18 to 20, which comprises an array of coloured trichromatic elements in which the trichromat is selected from: a red, green and blue trichromat; and a cyan, magenta and yellow trichromat.

22. A display which comprises a substrate according to any one of claims 18 to 21.

23. A display according to claim 22, which comprises a liquid crystal display.

24. A process for printing a substrate with a composition according to any of claims 4 to 12 using an ink-jet printer.

25. A cartridge suitable for use in an ink jet printer containing an ink according to any one of claims 4 to 12.
26. A paper, overhead projector slide, textile or colour filter printed with a composition according to any one of claims 4 to 12.
27. A colour filter comprising red, green and blue filter elements, or yellow, magenta and cyan filter elements, characterised in that the filter carries a compound of Formula (1) as defined in claim 4.